Study on stabilization of pvc In the presence of (Ho,Tb and Dy) stearate by uv-visible spectroscopy

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Abstract

This study describes preparation of three metal carboxylate complexes, holmium stearate,Terbium stearate and Dysprosium stearate,which are used as thermal stabilizers for pvc.These complexes are identified by their infrared spectra, elemental analysis and by DSC technique.

It is found that these complexes have some indication for same transition of polymers have liquied crystal properities.

Uv-Visible spectra are used to study the thermal unstabilized pvc and stabilized pvc degradation of reprecipitated from THF by methanol. This was done by the investigation of the absorption of the polymers resulted from the losing of HCL from the polymers chain at 275 and 385 nm, which were corresponded to three and seven conjugated double bonds respectively.

Mechanisms for thermal stabilization process of prepared complexes have been suggested, these stabilizers reduce the autocatalysis for hydrogen chloride or formation of esteric bonds on polymer chain or formation of coordination complexes.

Introduction

It is known that the degradation. of poly vinyl chloride resins is due primarily to a zipperlike elimination of hydrogen chloride which gives rise to pigmented and easily oxidizable ,polyenes. A number of workers have argued that' the elimination is autocatalyzed by hydrogen chloride, others contend that autocatalysis occurs only in certain atmospheres, while the most evidence appears to make doubtful any hydrogen chloride catalysis [1,2].

The susceptibility of PVC to degradation is attributed to the defective chemical structure of the polymer. These defects include allylic chlorine in the chain, end groups, copolymerization of oxygen during polymerization, and probably head to head structure and chloromethyl side chain branching [3,4] , So that the addition of the stabilizers are considered an important and necessary process. It has generally been assumed that a major function of added stabilizers is to absorb hydrogen chloride, other functions being :

1- to add to conjugated polyene structures, by a Diels-Alder reaction.

2- to serve as antioxidants and thus protect the polymer molecules from harmful oxidation.

3- to act as filters or screens against photoinitiated degradation [5,6].

On the other hand, elucidations of the stabilization effect of carboxylates in PVC are mostly based on the work of

Frye and Horst of 1959 [7], who suggest that the so-called labile chlorine atoms in the polymer chain (i.e., those adjacent to double bonds) are substituted by carboxylate groups, with the formation of esteric bounding. The ester groups are assumed to be bonded to the chain more strongly than the chlorine atoms, thus preventing additional splitting-off of hydrogen chloride, which occurs by the Zip mechanism [8,9].

The aim of this paper is to study the effect of Holminum stearate, Terbium stearate and Dysprosium stearate on the thermal degradation of Pvc using the visible-ultraviolet spectra.

Experimental

1- preparation of chemicals

The poly vinyl chloride employed (petrochemical company, Basrah,Iraq) has following characteristics ;

(scc 676, K.value =76.5-65:5, Density (g/cm^3) = 0.45, Ash content=0).

It was purified by addition of tetrahydrofuran and then precipitated by the addition of methanol. It was dried in air and then in vacuum at room temperature [3].

The Holmium stearate ; was prepared as following [10]:

4 g of Stearic acid was dissolved in 100 ml potassium hydroxide (0.14 M), then 100 ml of (0.05 M) Ho(N03)3 was added gradually with stirring. precipitate of Ho-stearate was formed. The precipitate was filtered then washed for several times with distilled water, next with methanol.

It was dried under vacuum at 40 ^{o} C. Tb-stearate and Dy-stearate Also prepared at the same method and with -a stability of used metal salt moles.

2- Preparation of samples of stabilized PVC

The stabilized samples were prepared by mixing of 0.02 g of prepared stabilizers with 1.0 g of pvc (W:W=2%).

Absorbances at 275 and 385 nm were used to study the thermal degradation of unstabilized pvc and the reprecipitated pvc from the stabilizer. [11]

Complexes identification

1- Differential Scaning Calorimetry (DSC).

Table(1) show the melting rang of study complex metals. The ubnormal properties in this table is the wide rang of melting this complexes. in fact these complexes proceed across transition state during the melting and become with attributed jelly;structure then translates to clear liquid at melting point, like this behavior was observed from researchers [9,12],it was showed that the Barium stearete which melts at180c was associated with crystalline phase transition(mezo form)at 150c which converted from three dimensional plat structure to structure like rods. Also the cadmium streate and calcium streate have liquid crystal properties represented by crystal transition (bezo form) at 99c and 180c respectively in other hand,Zinc streate havnt this property. To recommended this observed state in study complexes the DSC analysis have been done as shown in figures (1-3) and table (2).

2- Elemental analysis and infrared spectra

The metal complexes were identified by elemental. analysis (CHNS-O-EA1108-Elemental analyzer, college of science, Al-Nahrain Univ.). The results show that the practical ratio of carbon and hydrogen are equal to theoretical values as shown in table (1) except some differences which are attributed to experimental errors.

Also these complexes identification by there infrared spectra (SP3 - 300 infrared spectro photometer, college of science, Basrah university) as shown in tables (3,4) and figures (4,5).

Table (1): The expected formula and elemental analysis results of prepared metal stearates

Complex	Formula	Elemental analysis				Milting point (^{o} C)
		Theoretical %C	Practical %C	Theoretical %H	Practical %H	
Ho-stearate	$[Ho(CH_3(CH_2)_{16}COO)_3(H_2O)_2]$	61.63	61.61	10.36	10.29	120 – 210
Tb-stearate	$[Tb(CH_3(CH_2)_{16}COO)_3(H_2O)_2]$	61.98	61.88	10.40	10.47	109 – 130
Dy-stearate	$[Dy(CH_3(CH_2)_{16}COO)_3(H_2O)_2]$	61.77	61.71	10.39	10.43	113 – 228

Table (2): DSC data for prepared complexes

Complex	Temperature (^{o} C)	Temperature of peak (^{o} C)	H (J/gm)
Ho-stearate	80.3 – 100 105.5 – 136 230.5 – 260	95.7 130.5 250.3	1.83 48.3 1.34
Tb-stearate	63.7 – 126.5	106.7	120.6
Dy-stearate	94 – 126.9 272 – 297	114 280.3	29.5 9.44

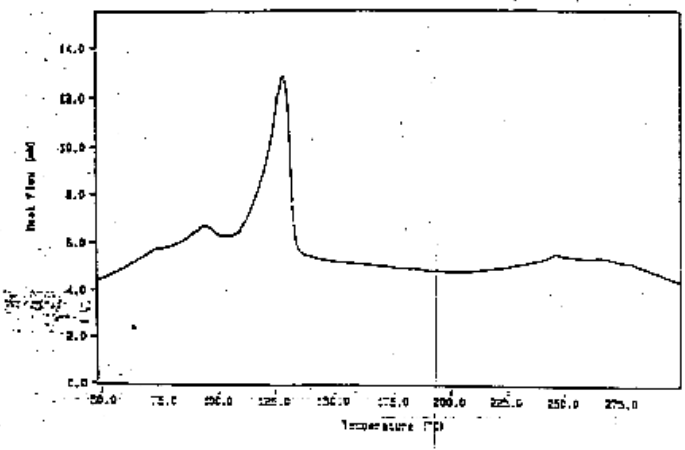

Fig.1: DSC spectrum of Ho-Stearate

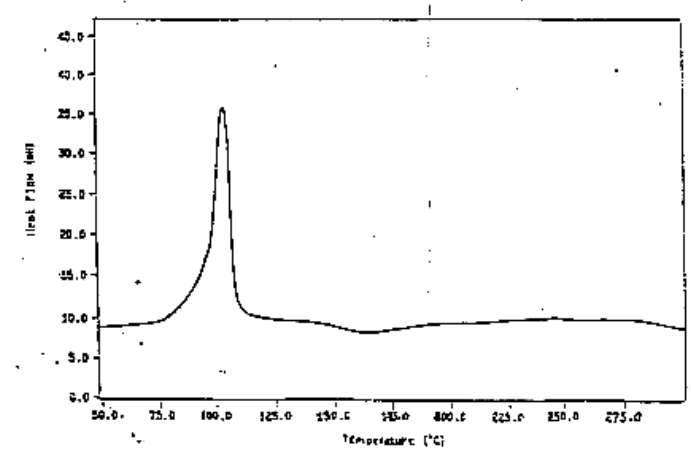

Fig.2: DSC spectrum of Tb-Stearate

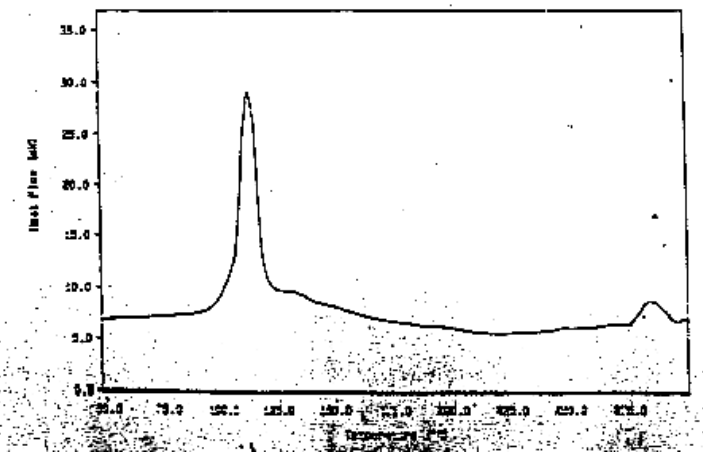

Fig.3 : DSC spectrum of Dy-stearate

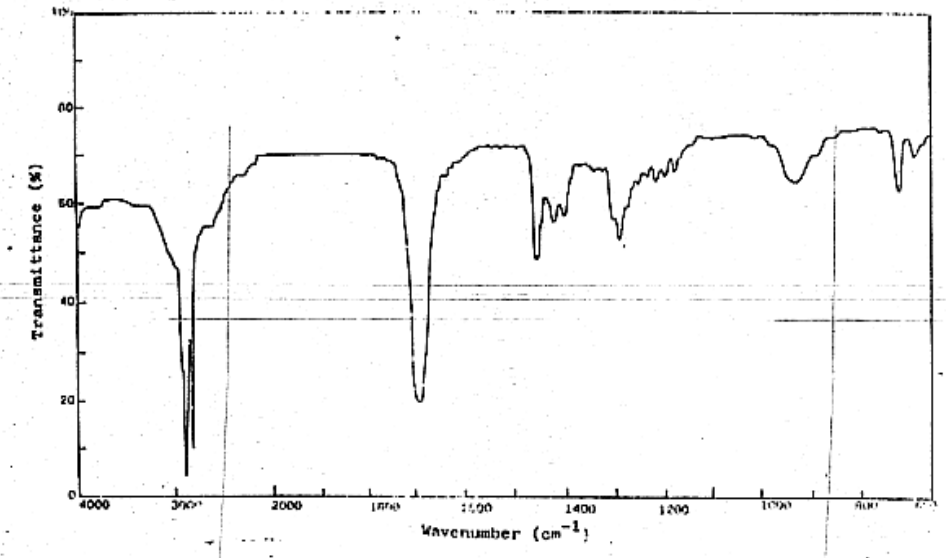

Fig.4: Infrared spectrum of stearic acid

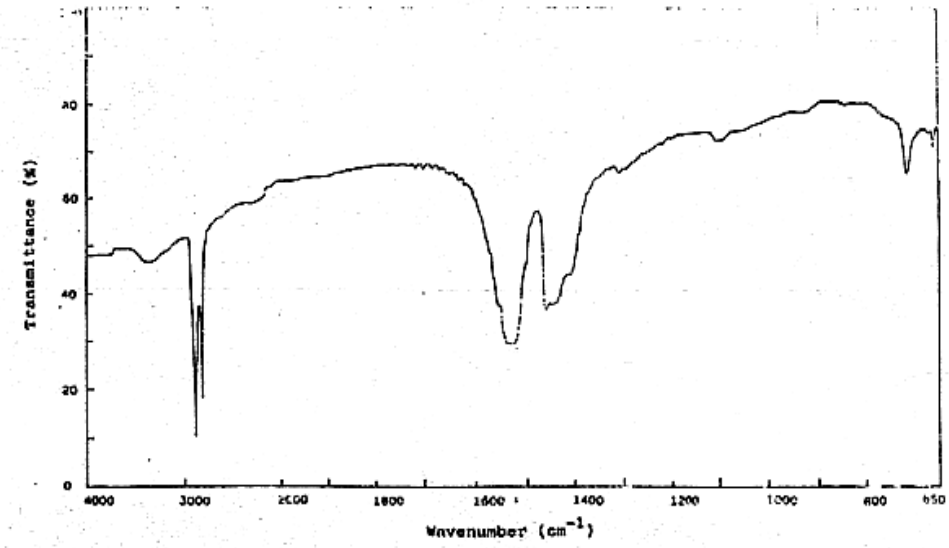

Fig.5: Infrared spectrum of Ho-Stearate

Table (3): Data of infrared spectrum of stearic acid
s=strong , m=medium

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})	Bending vibration of C-H (cm^{-1})
Stearic acid	**2640-3300 (s)**	**2920 (s) 2900 (s) 2825 (s)**	**1960 (s)**	**1405 (m) 1425 (s) 1460 (m)**	**933 (m)**	**1290 (m) 1256 (m)**	**720 (m)**

Table (4): Data of infrared spectrum of metal carboxylates
s= strong, m= medium, w= week

Complex	Stretching vibration of O-H (cm^{-1})	Stretching vibration of C-H (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})
Ho-stearate	**3400 (m)**	**2920 (s) 2900 (s) 2830 (s)**	**1523 (s)**	**1445 (s)**	**936 (w)**	**720 (m)**
Tb-stearate	3400 (m)	**2920 (s) 2900 (s) 2830 (s)**	**1525 (s)**	**1440 (s)**	**938 (w)**	**720 (m)**
Dy-stearate	3400 (m)	**2920 (s) 2900 (s) 2830 (s)**	**1526 (s)**	**1445 (s)**	**935 (w)**	**720 (m)**

Discussion

The polyvinyl chloride undergoes thermal decomposition when exposes to high temperature during the industrial process leads to losing hydrogen chloride gas and formation of conjugated double bond (polyenes) with different lengths and separated unconjugated double bonds [13].

At one study the total number of double bonds in pvc were calculated by ozone absorption, it was found that the formation of short polyenes (2 to 4) conjugated double bonds is the more probability [14].

Other studies[15,16] show that the polyenes become more active in the secondary reactions leading to form crosslinking and aromatic purolysates which cause undesirable chang in the properties of polymer, therefor the addition of stabilizers is important.

In this study uv-visible obsorption is used to follow the changes that happen in polyenes chain during the exposes process to thermal strain of unstabilized pvc and reprecipitated pvc prepared from metal carboxylates like Holmium stearate,Terbium stearate and Dysprosium stearate.

Fig.(6) show that there are more than one peak in the spectra which indicate that there are more than one coordinate form in polyenes. To study the thermal decomposition process easily it was limited tow region at 275 nm and 385 nm. the absorbence on this two region corresponding the formation of three and seven conjugate double bonds respectively [8,11].

Fig.(6) and table (5) show that the intensity of absorption at 275 nm is more than at 385 nm..Concluding from that, the concentration of triplet polyenes in the polymer chain is more than haptalet polyene and that is expected because the triplet polyenes start formation since the initial expose to thermal strain.

It also shows from the spectrum that there is an increase in absorbance intensity for all wave lengths conjugated with increase in exposes period to thermal strain refers to the different consists which increase with time in polymer chain.

In addition to that, conclude from the comparison of absorbent beams intensity at 275 nm and 385 nm for unstabilized pvc and reprecipitation pvc that the prepared complexes able to increase the thermal stability for pvc by reduce the conjugated double bonds that result from the liberation of hydrogen chloride.

Figs.(7),(8) show the relationship between the polyenes absorbence to unstabilized pvc and reprecipitation pvc and the exposes period for thermal strain at 275 nm and 385 nm, and show areducing in absorbance intensity in stabilized pvc samples comparison with unstabilized pvc which indicate that these stabilizers reduce the exist of the triplet and seventh conjugated double bonds in polymers chain, which illustrated the efficiency of these stabilizers in stabilized the polyvinyl chloride.

On the other hand the action of prepared carboxylic acid in thermal stability process follow the following mechanism.

1- the carboxylats react with liberated hydrogen chloride from the chain of polymer and that prevent the catalytic effect of HCL.

M (RC02)3 +HCL ⟶ MCl(RC02)2+RCOOH

MCl(RC02)2+HC1⟶ MC12RC02+RCOOI I

MCL2RC02+HC1 ⟶ MC13+ RCOOH

Where:

R=CH3(CH2)16,M=Ho,Tb,Dy

2- the carboxylats react with chain of the polymer by forming esteric bonds and the stabilization process due to that the excitation energy to separate carboxyl group is more than for losing HCL.

3- Lanthanids metals are able to form complexes by coordinated bonding with chloride atoms in systematic polymer chain or with allyle chloride atoms in chain which contains unconjugated double bonds or conjugated double bonds.

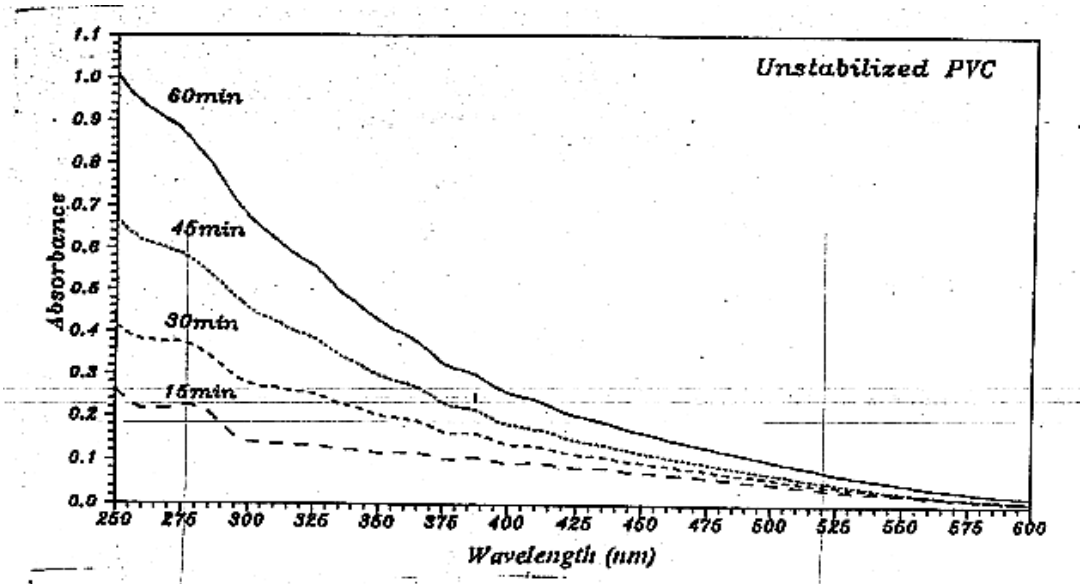

Fig.6: Ultraviolet - visible spectra of unstabilized PVC at different periods of thermal degradation at 240 °C.

Table (5) : Show the absorbance values at 265 nm and 385 nm for unstabilized pvc reprecipitated pvc from Ho , Tb and Dy carboxylate in THF solvent

Absorbance at 385 nm				Absorbance at 275 nm				Compound
Thermal strain time (min)				Thermal strain time (min.)				
60	45	30	15	60	45	30	15	
0.305	0.218	0.161	0.106	0.873	0.583	0.375	0.222	Unstabilized
0.260	0.182	0.118	0.071	0.777	0.531	0.229	0.156	Pvc + Ho-stea
0.270	0.196	0.127	0.079	0.781	0.536	0.325	0.174	Pvc + Tb-stea
0.287	0.189	0.112	0.075	0.821	0.481	0.310	0.194	Pvc + Dy-stea

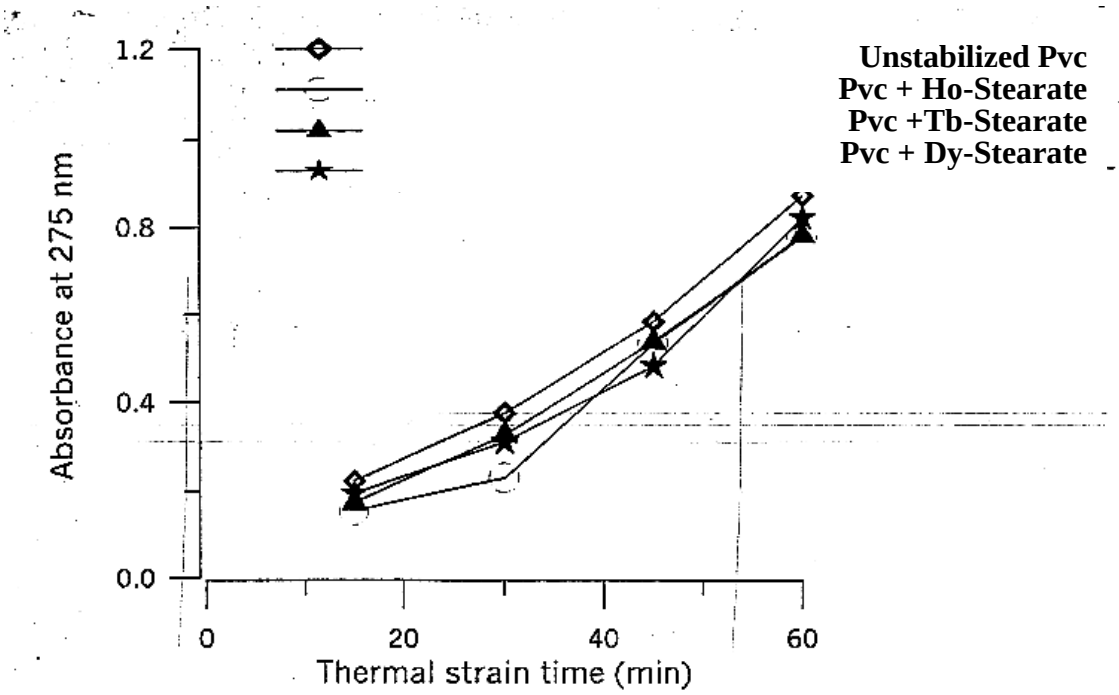

Fig.7: Absorbance at 275 (nm) of compounds at different thermal strain time(min)

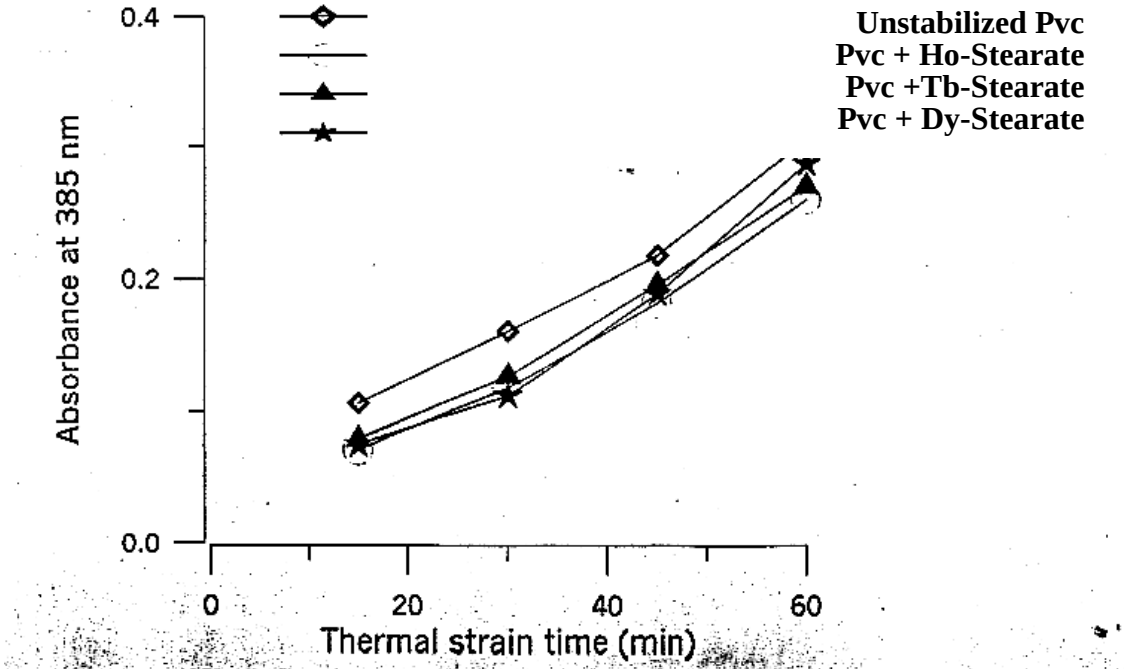

Fig.8: Absorbance at 385 (nm) of compounds at different thermal strain time (min)

الخلاصة:-

تضمنت هذه الدراسة تحضير ثلاثة معقدات فلزية كاربوكسيلية مثل سترات الهولميوم، سترات التربيوم وسترات الدايسبروسيوم والتي استخدمت كمثبتات حرارية للبولي فانييل كلورايد.

هذه المعقدات شخصت بطيف الاشعة الحمراء وتحليل العناصر بالاضافة الى المسح المسعري التفاضلي، لقد وجدت مؤشرات تعود لوجود نفس الانتقالات التي تحدث في بعض البوليمرات التي تمتلك صفات البلورات السائلة.

استخدم طيف الاشعة المرئية – فوق البنفسجية لدراسة البولي فانييل كلوريد الغير مثبت حرارياً وانحلال Pvc المثبت المعاد ترسيبه من THF باستخدام الميثانول، وهذه الدراسة تمت ببحث الامتصاصية للبوليمر الناتج من فقدان HCl من السلسلة البوليمرية في 275 و 385 نانومتر، والتي تطابق الاواصر المزدوجة المتبادلة(3و7) على التوالي.

تم اقتراح عدد من الميكانيكيات لعمليات الاستقرار الحراري للمعقدات المحضرة. هذه المثبتات تقلل من التحفيز الذاتي لكلوريد الهيدروجين او تكوين اواصر استيرية على السلسلة البوليمرية او تكوين معقدات تناسقية.

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