IBN AL- HAITHAM J. FOR PURE & APPL. SCI. VOL.19(4) 2006

IR and Uv-Visible Study of the Thermal Stabilization for pvc Stabilized with (Ho,Tb and Dy) Stearate and Synergistic Mixtures

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Abstract

Three types of metal carboxylates (Ho,Tb and Dy) stearates were used as thermal stabilizers for PVC. Infrared spectra (1500-1900 cm^{-1}) were studied for PVC films stabilized with these metal carboxylates. Two types of oxygen were found –containing products that were formed during the thermal degradation .On the other hand , the presence of atmospheric oxygen leading to the formation of carbonyl groups on the chain seems to play a great role in the stabilization of PVC. It was found that IR spectroscopy was suitable to follow the consumption of the carboxylates within the thermal stress periods via antisymmetrical stretching vibration of COO. The thermal stability for the PVC in present of synergistic mixtures (Ho-Tb,Ho-Dy and Tb-Dy) stearates was studied by Ultraviolet-visible spectra.The results indicate that these mixtures have considerable stabilization efficiency for the PVC.

Introduction

The degradation of PVC is due to azipperlike 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 occures only in certain atmospheres , while the most evidence appears to make doubtful any hydrogen chloride catalysis. (1,2)

The degradation has been studied by various workers and three different mechanisms based on different active centers mainly radical, ionic and molecular have been suggested (3). This susceptibility of PVC to degradation is attributed to the defective chemical structure of the polymer. These defects include allylic chlorine in the chain (4), copolymerization of oxygen during the polymerization (5) and probably head to head structure and chloromethyl side chain branching (6).

The synergistic effect of mixed metal carboxylates has been studied by many workers (7,8). Synergistic stabilization of some binary mixtures of carboxylates in PVC seems to be connected with the intraction or complexation of both components. The problem of interaction of these two types of carboxylates has not been studied systematically , but very interesting results were reported on the complexation of Na and Zn stearates(8).

The aim of this paper was to study efficiency of metal stearates in question and their synergistic effect in the thermal stability for PVC using the infrared and ultraviolet-visible spectroscopy.

Experimental

A – Poly (vinyl chloride) (PVC)

Powder pvc sample obtained from The Petrochemical Campany , Basrah, Iraq and has the following characteristics:

Scc 676 , K. value = 76.5-65.5 , density (g/cm^3)=0.45 , ash content = 0

PVC was purified by forming a solution in pure THF and reprecipitating it using methanol.

The sample was dried under vacuum at 70 °C

B – Metal stearates

The (Ho, Tb and Dy stearates) were prepared according to our recent paper and were identified by elemental analysis , infrared spectra and DSC technique (11).

C – The samples of stabilized pvc

The stabilized samples were prepared by mixing 0.03 g of metal **stearates** (stabilizers) at singly with 1.0 g of PVC (w : w = 3%) . IBN

The infrared spectra (1500-1900 cm^{-1}) of pvc films at different periods of oxposure to thermal stress at 250 °C were recorded (7,10).

The synergistic effect of these metal stearates was studied by mixing 0.15 g of each two metal stearates with 10 g of PVC by grinding the required amount in an agate mortar for 15 minutes , and then ultraviolet-visible spectra at 275 and 385 nm were used to study the thermal degradation of unstabilized pvc and the reprecipitated pvc from the stabilizers (synergistic mixtures) (12).

Results and Discussions

A – Infrared spectra

In order to study metal stearates or their effects in pvc by infrared spectroscopy , one must choose the film thickness to give sufficient absorption in appropriate ranges-the IR spectra did not study the changes that took place in the same polymer chain because most absorption bands of pvc alone were strong and can not follow the changes in intensity , so that the present work determined two spectral ranges of IR spectrum; spectral ranges (1500-1600 cm^{-1}) and (1700-1750 cm^{-1}) .

In order to carry out the quantitative study of IR spectra , we have calculated the absorbances of the bands during the following equation (13):

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

Where

A_i : absorbance at wavenumber under study

T_{1800} : the percentage of transmittance of 1800 cm^{-1} which is considered as the base of measurement.

T_i : The percentage of transmittance at the studied wavenumber.

The spectral range (1500-1600 cm^{-1})contains absorption bands of the antisymmetrical stretching vibration of the COO^- group . The position of band is determined by the bound cation:Ho-stearate lies at 1523 cm^{-1} , Tb-stearate at 1525 $cm^{-1}$and Dy-stearate at 1526 cm^{-1}. It is possible to follow the decrease in the absorption of this band during the degradation and to derive conclusions about the consumption of the stearate (13). The changes are quantitively represented in figures (1-8). The variations of the intensity of the COO^- group in all metal stearates in this study through the subjection of the sample of stabilized PVC for Thermal stress as a result of the reaction of stearates.

with hydrogen chloride liberated from the polymer or esterification reaction (14).

The spectral range (1700-1750 cm^{-1}) belongs to the stretching vibration of carbonyl group. The two bands in stabilized pvc spectra at 1735 cm^{-1} and 1700 cm^{-1} were noticed , and this is because of the formation of two forms bearing oxygen during the exposure to the thermal stress.

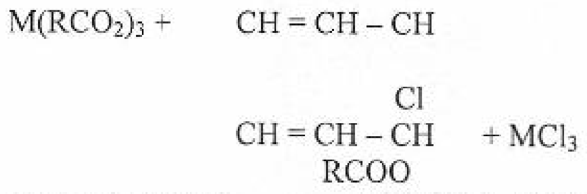
In addition , the band at 1735 cm^{-1} attributed to the formation of ester groups in the pvc chain , and the band 1700 cm^{-1} is due to the carbonyl group bound to pvc (14,15). The changes in these bands are shown in figures (1-8)

B – Ultraviolet-visible spectra

PVC undergoes thermal decomposition in the presence of heating , losing hydrogen chloride gas . This thermal decomposition leads to the formation of conjugated double bonds of different longs . These bonds are active in side reactions that lead to the formation of crosslinking and aromatic pyrolysates, and as a result give unwanted changes in the properties of the polymer , thus, the addition of thermal stabilizers to the PVC will be necessary and important.

Ultraviolet-visible spectra were used in this study to follow the occurred changes in the chains of the polymer during thermal strain for the unstabilized PVC and reprecipitated PVC from the synergistic mixtures. In order to facilitate the ability of following the thermal decomposition of PVC through the absorbance of formed double bonds, the study was made at 275 and 385 nm, because the absorbance at these wave lengths corresponds to the formation of three and seven conjugated double bonds respectively (12 , 13).

The efficiency of stabilization of these synergistic mixtures can be explained by the following equations (16) :



$$M(RCO_2)_3 + CH=CH-\underset{Cl}{CH}$$

$$CH=CH-\underset{RCOO}{CH} + MCl_3$$

$MCl_3 + N(RCO_2)_3$ --------- $M(RCO_2)_3 + NCl_3$

Where

M: first metal N: second metal

From the above equations, $M(RCO_2)_3$ have ability to sumbit to esterification reaction with the polymer chain to form (MCl_3) which acts as lious acid that hastens the dehydrochlorination but the existence of $N(RCO_2)_3$ leads to the change of (MCl_3) into inactive (NCl_3), then the reesterification process takes place that leads to the increasing of thermal stability.

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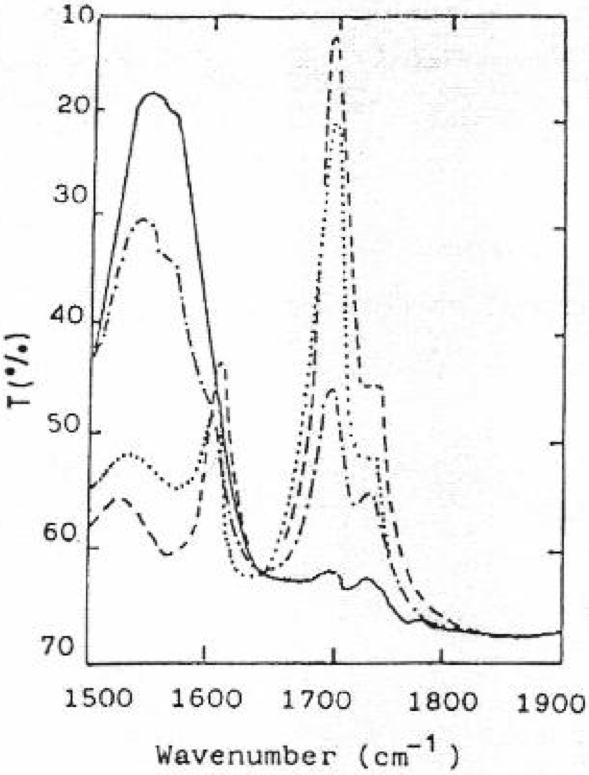

Fig. 1 : Infrared spectra of PVC stabilized with Ho-stearate after 25 min —— ; 35 min –·–· ; 45 min ..... ; 55 min ---- of decomposition at 250 ° C in air

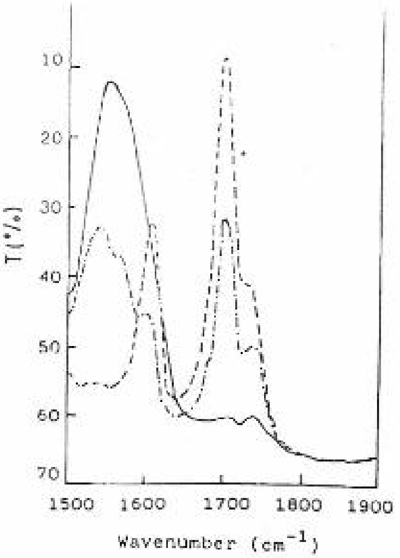

Fig. 2 : Infrared spectra of PVC stabilized with Tb-stearate after 25 min —— ; 35 min —·— ; 45 min ------ of decomposition at 250 ° C in air

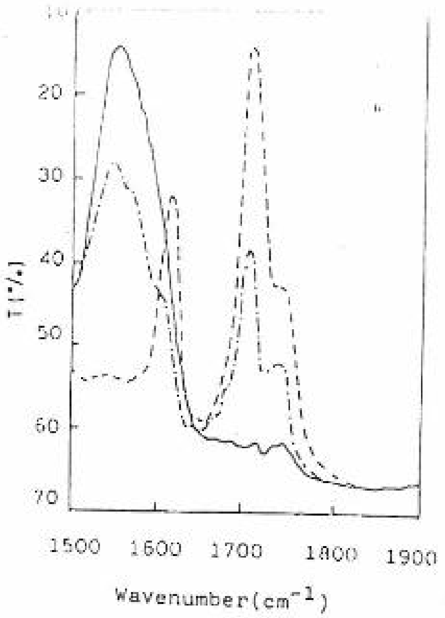

Fig. 3 : Infrared spectra of PVC stabilized with Dy-stearate after 25 min —— ; 35 min —·— ; 45 min ------ of decomposition at 250 ° C in air

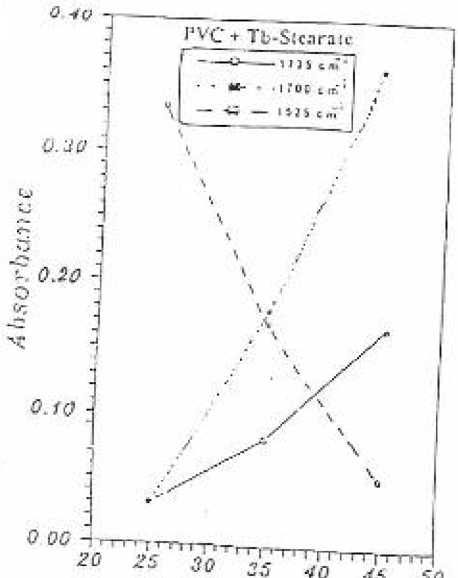

Fig . 5 : Dependence of the peak absorbances for PVC stabilized with Tb-Stearate on the time of thermaldegradation at 250 ° C in air { $A_i = \log(T_{1800}/T_i)$ }

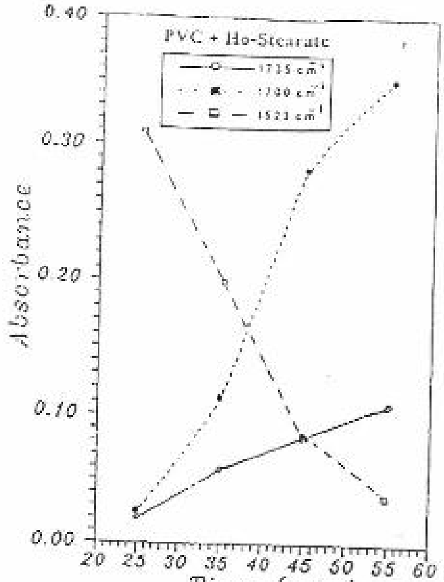

Fig . 4 : Dependence of the peak absorbances for PVC stabilized with Ho-Stearate on the time of thermal degradation at 250 ° C in air { $A_i = \log(T_{1800}/T_i)$ }

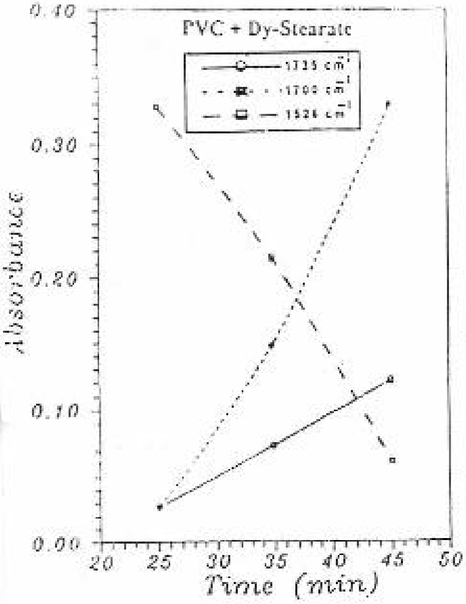

Fig . 6 : Dependence of the peak absorbances for PVC stabilized with Dy-Stearate on

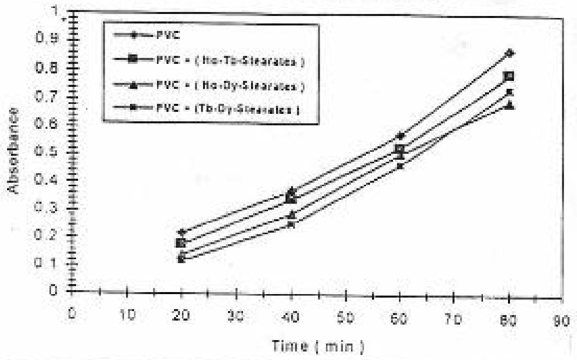

Fig . 7 : Dependence of absorbance of PVC at 385 nm on the time of thermal degradation at 250 ° C

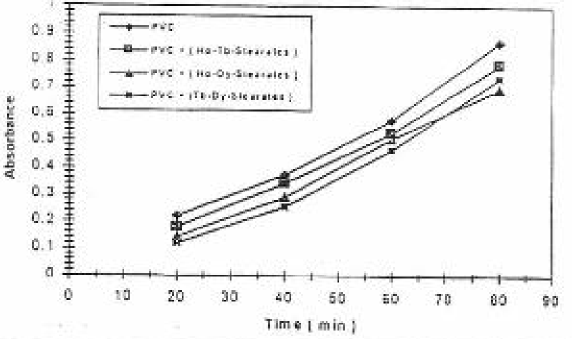

Fig . 8 : Dependence of absorbance of PVC at 275 nm on the time of thermal degradation at 250 ° C

دراسة اطياف الاشعة تحت الحمراء والاشعة المرئية وفوق البنفسجية لعملية التثبيت الحراري للـــ PVC المثبت بستيرات كل من الهولميوم والدبسيبرسيوم وامزجتها التعاونية

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استخدمت في هذه الدراسة ثلاث كاربوكسيلات فلزية وهي ستيرات كل من الهولميوم والتربيوم والدبسيبرسيوم كمثبتات حرارية للـــ PVC حيث تم دراسة اطياف الاشعة تحت الحمراء ضمن المنطقة الطيفية (1500-1900) سم$^{-1}$ لافلام الـــ PVC المثبت بوساطة تلك الكاربوكسيلات الفلزية وقد وجد ان هناك نوعين تتكون من النواتج المحتوية على الاوكسجين خلال عملية التفكك الحراري ومن جانب اخر وجد ان الاوكسجين الجوي له دور في تكوين هذه النواتج ولاسيما مجاميع الكاربونيل على السلسلة البوليمرية والتي تبدو انها تلعب دوراً كبيراً في عملية التثبيت الحراري ومن ثم يمكن اعتبار مطيافية الاشعة تحت الحمراء وسيلة ملائمة لمتابعة استهلاك الكاربوكسيلات في اثناء تعرضها للحرارة بواسطة متابعة حزمة الاهتزاز الاتساعي غير المتماثل للمجموعة (COO^-).

كما تم دراسة اطياف الاشعة المرئية وفوق البنفسجية لعملية التثبيت الحراري للـــ PVC بوجود الامزجة التعاونية لتلك الكابوكسيلات حيث اشارت النتائج ان تلك الامزجة تمتلك كفاءة تثبيت جيدة للـــ PVC .