Effect of thermal stabilizers (Ba/Cd/Zn metal salts carboxylate and dibasic lead stearate), on the photodegradation of PVC films.

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ملخص :

أجري تحلل الضوئي من البولي فينيل الكلوريد (PVC) المحول بعد إضافة عامل الاستقرار لثنائي قاعدة الرصاص (DLS) وخليط من الأملاح المعدنية ل (Ba/Cd/Zn) . قد أجري بواسطة طرق التحليل الحرارية :التحليل اللانتالبي التفاضلي (AED) والتحليل الحراري الكتلي (ATG) . إن التحليل AED سمح بملاحظة أن إضافة عوامل الاستقرار للـ PVC يؤثر على التصرف الحراري للـ PVC ولهذا فإن ثمانية (8) خلائط قد حضرت لهذا الغرض. وقد تبين أن DLS و Ba/Cd/Zn الذين هما في الأصل مثبتين حراريين يساعدان على استقرار الـ PVC بطريقين مختلفين. أثناء التحوّل للـ PVC على شكل رقائق فإن المثبت الأول يستهلك جزئيا بينما المثبت الثاني يستهلك تقريبا كليا . إن التحليل الحرار ي التفاضلي المسحي و قياس زمن بداية التأكسد (TIO) قد بين ان تركيز ل DLS المتبقي بعد التحول يتفاعل مع الضوء UV هذا الذي يؤدي إلى إستهلاكه التدريجي مع زمن التعرض . إن قياسات الزمن (TIO) قد بينت أيضا أن كمية قليلة من Ba/Cd/Zn التي لم تكتشف بالطرق الأخرى الإكتشافية تتبقى بعد تحول ال - PVC. إن تأثير كل واحد من المثبتين و خلائطيهما المختلفة على استقرار ال PVC قد نوقش على ضوء تحليل النتائج المحصل عليها بـAED، ATG وTIO.

الكلمات المفتاحية *:PVC - الأشعة فوق البنفسجية - التحلل الضوئي - المثبت الحراري - التحليل الحرارو التفاضلي - قياس زمن بداية التأكسد - التحليل الحرارو الوزني*

Résumé

La photodégradation du polychlorure de vinyle (PVC) modifié par l'incorporation de stabilisants à savoir le stéarate dibasique de plomb (DLS) et un mélange de sels métalliques de (Ba/Cd/Zn) carboxylates, a été conduite au moyen de méthodes d'analyses thermiques : l'analyse enthalpique différentielle (AED) et l'analyse thermogravimétrique (ATG). L'AED a permis de constater que l'addition de stabilisants au PVC influe son comportement thermique. Ainsi, huit (8) formulations ont été préparées à cet effet. Il a été montré que le DLS et le Ba/Cd/Zn qui sont tous deux à l'origine des stabilisants thermiques opèrent différemment leurs actions stabilisatrices sur le PVC. Durant la transformation du PVC en film, le premier est seulement modérément consommé alors que le second l'est presque entièrement. L'analyse calorimétrique différentielle à balayage et la mesure du temps d'induction à l'oxydation (TIO) a montré que la concentration de DLS qui reste après la transformation réagit avec la lumière UV ce qui conduit à sa consommation progressive avec la durée d'exposition. Les mesures de (TIO) ont également révélé qu'une petite quantité de Ba/Cd/Zn non décelé par les autres méthodes de caractérisation reste après la transformation du PVC.

L'effet respectif de ces deux stabilisants et ceux de leurs différentes combinaisons sur la stabilité du PVC est discuté à la lumière de l'analyse des résultats obtenus par l'AED, l'ATG et le TIO.

Mots clés: *PVC - UV – Photodégradation – Stabilisant Thermique – AED – TIO - ATG.*

Abstract

The photodegradation of polyvinylchloride (PVC) modified by the incorporation of thermal stabilizers namely dibasic lead stearate (DLS) and a mixture of (Ba/Cd/Zn) metal salts carboxylate, was investigated by means of thermal analyses methods: differential scanning calorimetry (DSC) and thermogravimetry (TG). By using DSC it has been shown that the addition of stabilisers to PVC affects its thermal behaviour. Eight (8) different formulations have been prepared for this purpose. It has been shown that DLS and Ba / Cd / Zn, which are both heat stabilizers, operate differently their stabilization effects on PVC. During processing, the former is only moderately consumed, while the latter reacts almost entirely. The DSC analysis and the oxidative induction time (OIT) measurements have shown that the unreacted DLS concentration interacts with UV light leading to its progressive consummation with ageing time. OIT measurements have also revealed that a very small amount of unreacted Ba/Cd/Zn, not detected by the other characterization methods, remains after processing. The respective effects of each stabilizer and those of their different combinations on PVC stability were discussed in the light of DSC, TG and OIT measurements.

Key words: *PVC - UV – Photodegradation - Thermal stabilizer – DSC – OIT - TG.*

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1. INTRODUCTION

Poly (vinylchloride) (PVC) is one of the leading polymers both in diversity of application and total weight of finished product. PVC widespread acceptance by industry is due in part to the successful development of stabilizers for PVC, which is the last naturally stable polymer in commercial use. Therefore, the poor thermal stability of PVC requires the use of heat stabilizers for its processing. However, PVC is also very vulnerable to light and readily degrades once exposed to sunlight. The reaction, known as photooxidation, causes mainly chain scissions and chemical degradation. This, results in a diminution of the average molecular weight, a dramatic deterioration of the mechanical properties, as well as a diminution of the clarity of the products. The sensitivity of PVC products towards UV light is due either to the presence of chromophores introduced into the material via additives or to structural defects developing during polymerization and/or processing. They are responsible for light absorption leading consequently to photodegradation. Even, if some disagreements still exist concerning the nature of the absorbing chromophores responsible of the initiation step, good potential candidates are postulated as for example: hydroperoxides, carbonyl groups, allylic chlorine, tertiary hydrogen, end groups such as double bonds (unsaturations and α-chlorinated short conjugated polyenes ...), metal salts(catalytic residues), and structural irregularities etc. All have been suggested as potential initiating chromophores [1 - 6].

Indeed, UV radiation has sufficient energy to cleave the C-C bond. However, the bonds that are primarily cleaved in the photolysis of PVC are the labile C-Cl bonds whose dissociation energy (approximately, 78 kcal/mol) would be increasingly lowered subsequently to a zipper-like elimination of HCl leading to the formation of conjugated polyenes sequences of progressive growing length. The colour change observable during ageing is due to the growth of these polyene sequences [1, 4, 7, 8].

In the presence of oxygen, PVC degradation becomes a complex oxidation process where oxidation products are formed. These products are characterized by IR spectroscopy with two characteristic absorption bands at 1720 cm^{-1} and at 3500 cm^{-1}, corresponding to carbonyl groups and hydroperoxides respectively. It is somewhat difficult to identify all the photoproducts constituting the complex and composite absorption band of the carbonyl groups. Many possible candidates have been still identified among them one can mention: carboxylic acids, α and β chloroketones, α and α' dichloroketones, acid chlorides, ester groups, peracids, peresters unsaturated ketones and lactones [4, 9 - 11].

Elsewhere, it was demonstrated that the addition of stabilizers to PVC affects both the kinetic of the carbonyl groups formation and the types of oxidation products formed during photodegradation [12].

Thermal analysis methods are effective tools in PVC degradation studies. They give a good insight on the structural changes undergone by the polymer during ageing.

The resolution of PVC degradation by DSC is not an easy task since some commercial PVC resins are slightly crystalline and their melting occurs in the same temperature range as that of their dehydrochlorination. In spite of that, a DSC thermogram highlights on the physical effects of the degradation on PVC morphology, such as the disappearance of the fusion peak in the case of semi-crystalline structures or the drop of the glass transition temperature to lower values consequently to chain scission reactions.

The effects of stabilizers on PVC decomposition can be investigated by thermogravimetry. Of course, this method is not sensitive enough to be processed without elimination of volatile fragments as for example acid chloride or intermolecular cyclization [13, 14].

However, the amount and the rate of these eliminations give useful information on the efficiency of the stabilizer system.

Addition of heat stabilizers is mandatory in any PVC receipt to prevent the molecular decomposition of the material by heating and/or by shearing during processing.

Additives that have found practical application as thermal stabilizers for PVC include metal soaps of carboxylic acids, organometallic compounds and inhibitors of radical chain reactions [15].

The most widely used stabilization systems for PVC are different metal soaps of Pb, Cd, Ba, Ca and Zn carboxylates or stearates. Algerian plastic plants producing PVC tubes and pipes utilize mainly these types of stabilizers. For example, one can mention the ternary combination of Ba/Cd/Zn carboxylates or lead salts of dibasic or tribasic lead stearate.

Although, Ba/Cd/Zn soaps are more expensive than many other stabilizers they are still attractive owing to their physiological harmlessness. The generally adopted assumption that a good thermal stabilizer is also a good light stabilizer for PVC relies on positive results of photostability of mixtures containing efficient thermal stabilizers. Sometimes, they do not react entirely during processing and substantial proportions remain chemically unchanged in the final product [16]. Do the remaining concentrations of the unreacted stabilizers interacts with light to prevent further photodegradation of PVC or do they have in the contrary an adverse effect on the PVC photostability? What is their respective interaction on each other when compounded at different concentrations? Do they promote a synergistic or an antagonist effect on PVC stability? On the light of the DSC tests and the TG measurements performed in this work, it will be tried to answer these emblematic questions.

2. EXPERIMENTAL

2.1 PVC films preparation

The formulations used are the same than those used in a previous work [12]. The preparation methodology is as follows: a commercial PVC powder, supplied by the national company “ENIP” of Skikda, is manually mixed with various concentrations of the two types of stabilizers namely Ba/Cd/Zn carboxylate and dibasic lead stearate. The eight different formulations that have been prepared are reported in table 1. The respective concentration of each constituent is given in phr (part per hundred resins). For example, the preparation of PVC A has required the addition of 1 gram of LDPE to 100 grams of PVC powder.

The chemical composition of the two stabilizers is described below:

DLS: $(C_{17}H_{35}COO)_2Pb.2PbO$

Ba/Cd/Zn carboxylate: $Me(OCOR)_2$ where Me independently can be Ba, Cd or Zn

The mixtures were poured successively on a two rolls mill to achieve the mixing and to prepare preformed sheets. The sheets were then squeezed between two aluminum plates and shaped into thin films of 200 µm by means of a compression-moulding machine (Wabbash) under a pressure of 35000 Psi and at a temperature of 180 °C.

Table 1.The eight PVC formulations, the concentrations are given in phr.

	A	B	C	D	E	F	G	H
PVC	100	100	100	100	100	100	100	100
LDPE	1	1	1	1	1	1	1	1
Ba/Cd/Zn	0	1	1	1	1	0.5	2	0
DLS	0	0	0.5	1	2	1	1	1

In an industrial PVC recipe to improve heat resistance and to help processing an external lubricant is added. Generally, they are saturated fat alcohols or di-carboxylic acids. To avoid the saturation of the PVC’s IR spectrum with the signal of these additives, 1 Phr of LDPE has been added to each recipe to ensure lubrication. It was then checked that the presence of this small amount of LDPE does not affect the IR spectrum of virgin PVC film [12] and its thermal behaviour as well

2.2 Ageing

To achieve ageing, the films were exposed to artificial UV irradiations at a temperature of 70°C. The source of light is a high-pressure mercury lamp of 400 watts. The bulb of the lamp made of borosilicate acts as a filter to get rid of wavelength light below 300 nm (absent from the solar light spectrum).

2.3 Techniques

The thermal analyses were carried out on a differential scanning calorimeter (DSC) and on a thermogravimeter (TG), Mettler TA 3000 instruments. Both were interfaced to a computer, which automatically recorded the thermograms. In both cases, sampling was performed in the same way. A few milligrams (≈10mg) were taken from the film. For the DSC test, the sample was pressed in an aluminum pan. To perform the DSC analyses, the samples were heated either in an inert gaseous environment (N_2) or in air from room temperature (i.e. 25°C, below Tg) up to 400°C with a heating rate of 10°C/mn. On the DSC thermogram, the glass transition temperature (Tg), characteristic temperature of an amorphous polymer, was taken as the midpoint of the transition.

The DSC apparatus allows also the determination of the oxidative induction time (OIT). Such a method provides a comparative measurement of the degree or the level of stabilisation of each formulation. In this technique, the sample was heated with a heating rate of 10°C/mn in an inert gaseous environment (N_2) from room temperature up to 240 °C. This temperature was chosen well above the processing temperature, sufficiently high to reduce the testing time to a reasonable duration, but not too high to prevent an early degradation of the material. Once, the sample has reached the equilibrium temperature (i.e., 240°C in our case), the controller automatically switches purge gas environment to air at the same purging rate [17]. The change over point to air is taken as the zero time. The oxidative induction time is assessed by monitoring the abrupt exotherm departure from the base line.

The thermogravimetric analysis was performed first to assess the effectiveness of the stabilisation systems on the rate of dehydrochlorination of the unexposed films and secondly to control the effects of ageing on this same rate. The experiments were carried out from room temperature to temperature up to 400°C with a heating rate of 10°C/mn either in an inert gaseous environment (N_2) or in air.

From the thermogravimetric curves, the following characteristics were determined:

- The temperature at the maximum rate of dehydrochlorination (T_{peak}) which corresponds either to the inflexion point of the TG curve or to the maximum rate of dehydrochlorination on the derivative thermogravimetric curve (DTG).
- The relative weight loss which corresponds to the ratio of the total weight loss on the initial weight; it is given in percent (%).
- The half-life (T_{50}) temperature, defined as the temperature at which the sample has reached 50% of the total weight loss. Its corresponding time (t_{50}) is the time needed to raise the sample temperature from room temperature (25°C) to the corresponding temperature (T_{50}) [18].
- The total duration of dehydrochlorination (t_T): the time between the onset of the fall of the baseline and the early stabilization of the baseline.

3. RESULTS

3.1 Thermal analysis of virgin PVC film

\- *Before ageing:*

The first transition observable on the unstabilized and unexposed film thermogram corresponds to the glass transition temperature which occurs at 89°C. To control the incidence of the temperature rise on the PVC microstructure during the DSC test two successive scans were run under the same experimental conditions (i.e inert atmosphere and an heating rate of 10°C/min from room temperature to temperature up to 250°C). It was observed that Tg shifts from 89 to 92°C (i.e a global increase of 3°C).

If the same experiment is performed in air the same effect is observed but, with a smaller increase; $\Delta T = 2°C$.

Tg variations give a good insight on the microstructural changes undergone by PVC and the shift of Tg to higher values indicate that during the temperature rise crosslinking could occur.

This grade of PVC being highly amorphous no fusion peak is expected to appear on the DSC thermogram. Indeed, when the test is performed under inert atmosphere (i.e.N_2) an imposing exotherm appears around 280°C, the calorific energy released is around 1070 J/g. If the same test is conducted in air at the place of the exotherm appears an endotherm of smaller intensity and the calorific energy absorbed is about 145 J/g (Fig.1 a and b).

The exothermic peak is relevant to an oxidation process occurring in the absence of atmospheric oxygen. Consequently, it can be deduced that this reactive oxygen comes from oxygen molecules entrapped in the material during processing. Then, during the thermal analysis, these molecules oxidize the material.

The endothermic peak recorded under air can be due either to the fusion of an existing crystalline phase or to a dehydrochlorination process.

To check which of these two hypotheses is the most probable a second scan was run on the same sample. The cooling rate was the same than that of heating to allow an eventual recrystallisation if any. No peak appears in the second scan (Fig. 1 c) also, it can be concluded that the endothermic peak is more probably relevant to the dehydrochlorination process.

On figure 2 are sketched the thermogravimetric curves of PVC tested in inert atmosphere (Fig. 2 a) and in air (Fig. 2 b) respectively. The test was performed with the same heating rate than the one used in DSC. In both cases, the weight loss recorded exceeds

50%, it is about 55.57 % in N_2 and 50.87% in air. Weight loss corresponds to the release of HCl molecules. Dehydrochlorination starts at 235.6°C in inert atmosphere and at 223°C in air. Their respective T_{peaks} are recorded at 286°C and at 281.5°C. These temperatures occur at the inflexion point of the thermogravimetric curves and correspond to the maximal rate of dehydrochlorination on their corresponding derivative thermogravimetric curves (DTG). These results show that dehydrochlorination is more efficient in inert atmosphere.

The inverted S-shaped curves of the TG thermograms are characteristic of an autocatalytic process of dehydrochlorination and confirm the catalytic effect of released HCl.

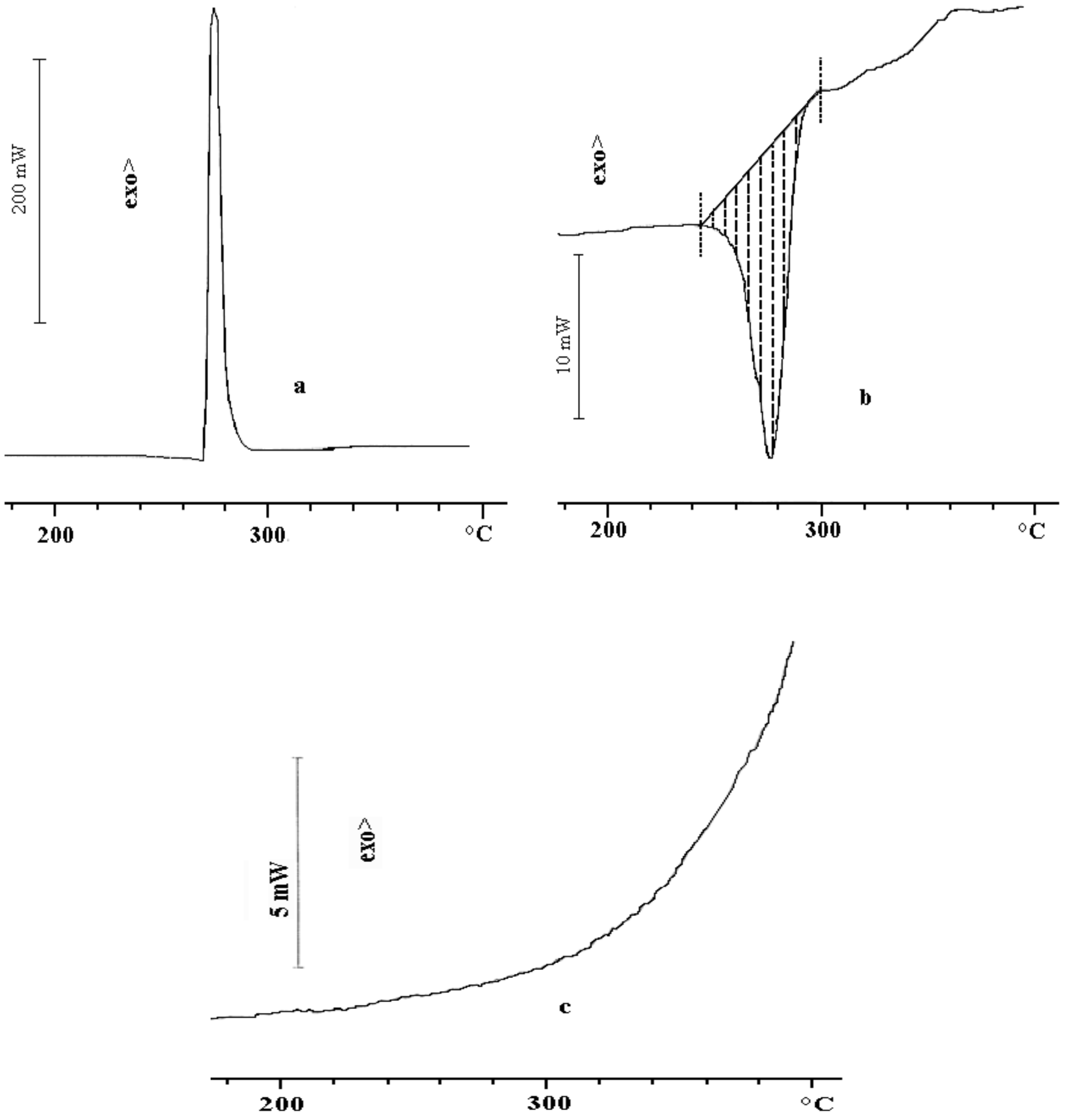


Figure 1. DSC thermograms of virgin unexposed PVC film a) under inert atmosphere b)under air, 1st scan c) under air, 2nd scan.

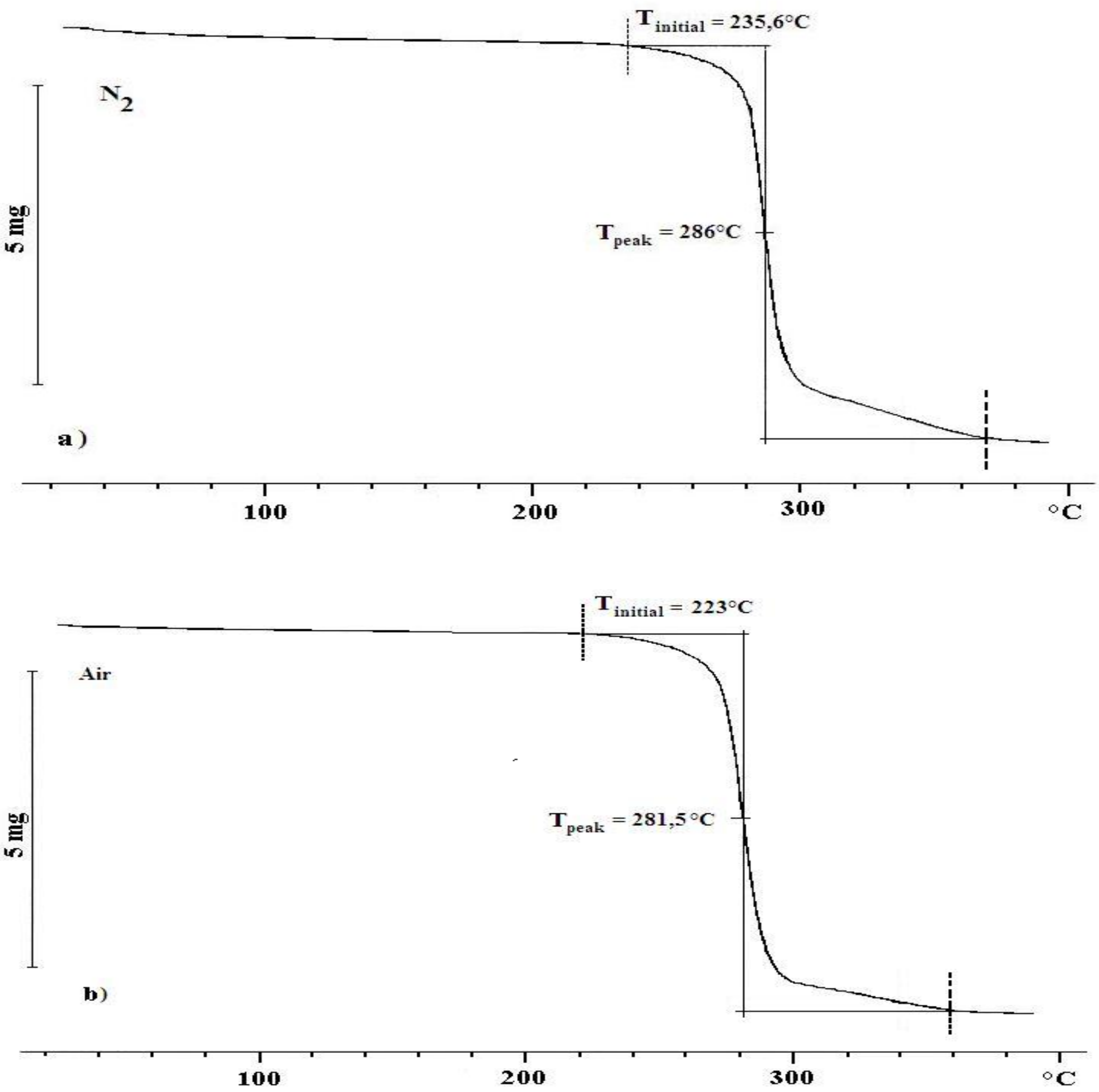


Figure 2. TG Thermograms of the unexposed virgin PVC film a) under inert atmosphere b) under air.

It is noteworthy that the weight loss in inert atmosphere is more significant and closer to the chlorine content of PVC (56%). Therefore, it can be assumed that the lower weight loss recorded in air is most probably due to the chemical reaction of atmospheric oxygen with the macromolecular chains consequently to a thermooxidative process occurring during the temperature rise. The addition of atmospheric oxygen to the polymeric chains lowers the total weight loss recorded by the apparatus. Under inert atmosphere, the thermooxidation occurs only with the entrapped oxygen initially weighed within the PVC sample. As such, there is no addition of extra oxygen atoms to the system; therefore, the weight loss recorded under inert atmosphere is closer to the chlorine content of PVC.

- *Effects of Ageing:*

For the aged PVC (50 h exposure), the glass transition temperature is recorded at 84°C. This value is lower than that of the unexposed film. The thermogravimetric test shows that the weight loss of aged PVC is about 49.87 % in inert atmosphere and 51.82% in air; T_{peaks} occur at 281.5°C and 287.5 °C respectively. The difference in the weight loss values for the measurements performed in the two different environments is this time less important than for the unexposed samples.

This smaller difference could indicate that the release of a small amount of HCl molecules could have already occurred during ageing reducing thus the variation of dehydrochlorination between the two experimental conditions.

3.2 Thermal analysis of stabilized PVC films

- *Before ageing:*

The Tg values of the eight formulations are reported in table 2. The addition of stabilizers to PVC slightly decreases Tg. The variation of this magnititude depends on the type and the concentration of the respective stabilizers. The lowering of Tg by miscible compounds (such as stabilizers) is known and has already been described [19].

Table 2. Glass transition temperature of each formulation

PVC	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Tg(°C)	89	84	85	83	85	85	81	86

In the temperature range (220-260°C) the addition of DLS to PVC affects the thermogram by the appearance of a small exotherm. The area of the peak increases with the stabilizer concentration (Fig. 3). An accurate observation of the curves allows us to postulate that i) the DSC analysis is sensitive to the presence of DLS ii) the sharpness of the small exotherm and its surface increases with DLS concentration iii) the temperature of its maximum shifts to higher values as well.

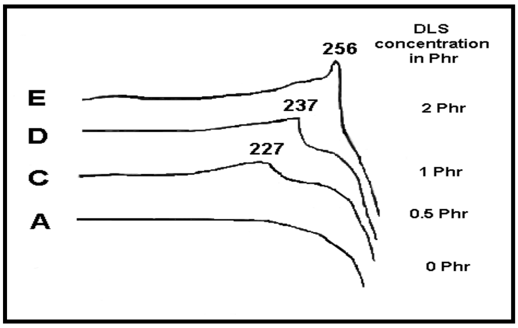


Figure 3. Effect of an increasing concentration of DLS (in PVC A, C, D and E respectively) on the DSC thermogram in the temperature interval (220-260°C).

- *Effects of ageing:*

On figure 4 are reported the variation of the Tg values of PVC B, D and H versus ageing time. These three mixtures represent the basic stabilisation systems of this study. In PVC B and H, each stabilizer is respectively used alone. PVC D is a combination of the two stabilizers mixed in the same proportion (Table 1). Therefore, these three formulations give a good insight on the respective action of each stabilizer and that of their proportional combination on Tg. It appears that Tg varies in a non monotonous manner in all cases.

The Tg of PVC B decreases slightly during the first 20h from 84°C to 83°C. Then, it increases almost linearly to reach 86°C at the end of the ageing protocol. The Tg of PVC H follows an U-shaped curve with a starting value of 86°C, a minimum value of 82°C and an end value of 89°C. For PVC D, Tg remains almost stable during all the duration of the ageing protocol excepted at the last stage of ageing where occurs a slight increase occurs. Globally in all the cases, Tg increases with ageing but the way and the rate differ from one formulation to another.

According to the precedent results and after a cursory examination of the DSC thermograms of the three formulations it appears that there are three distinguishable areas, which are sensitive to the effect of ageing. Those are mainly the glass transition region (around 80°C), the area in the temperature range (220-260°C) and the area above 260°C. In the following, the discussion will be essentially accessed on the analysis of these three distinguishable areas.

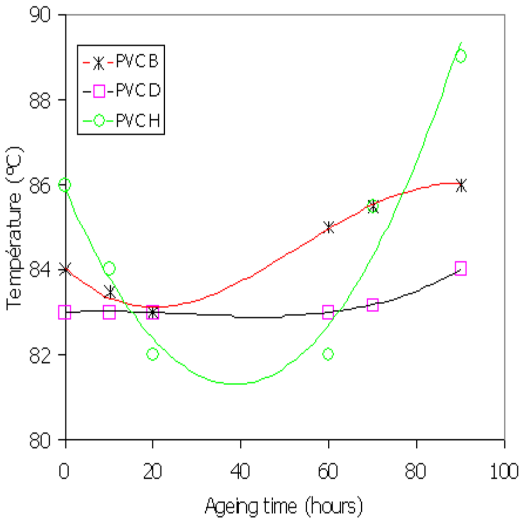


Figure 4. Variation of the glass transition temperature of PVC B, D and H with ageing time

In figure 5 (a, b, c) are sketched the portions of the curves corresponding to the glass transition temperature of PVC B, D and H for three ageing stages (20h, 60h and 90 h). It can be seen that the portion of the curve, which corresponds to the glass transition, becomes progressively a small endothermic peak of increasing area.

This phenomenon can be attributed either to internal stress relaxation caused by a physical ageing of the material or to crosslinking arising from photooxidative reactions [18].

Ageing has also affected the small exotherm, which appears in the temperature range (220-260°C) of mixtures containing DLS. In figure 6 are sketched this portion of the thermogram of PVC B, D and H for three ageing stages.

For PVC B stabilised only with Ba/Cd/Zn this maximum does not appear. This confirms well that this peak appears only with the presence of DLS.

PVC D and H, which both contain one (1) phr of DLS show that this small exotherm disappears gradually with ageing time.

Based on what is observable in figure 3 and figure 6, it can be postulated that the disappearance of this small exotherm corresponds to the progressive consumption of DLS. This hypothesis is supported by the fact that it coincides with the disappearance of its corresponding IR spectroscopic absorption band described elsewhere [12]. In fact, it has been shown that DLS does not react entirely during processing and that the IR absorption band around (1510-1540 cm^{-1}) belonging to the unreacted concentration disappears progressively with ageing time.

On figure 7 are reported the last portion of the DSC curves of PVC B, D and H. For all the unexposed mixtures, in the temperature range above 260°C a broad exothermic peak appears, similar to that of virgin PVC film. With ageing and according to the case, it occurs either a peak inversion or an intermediate behaviour.

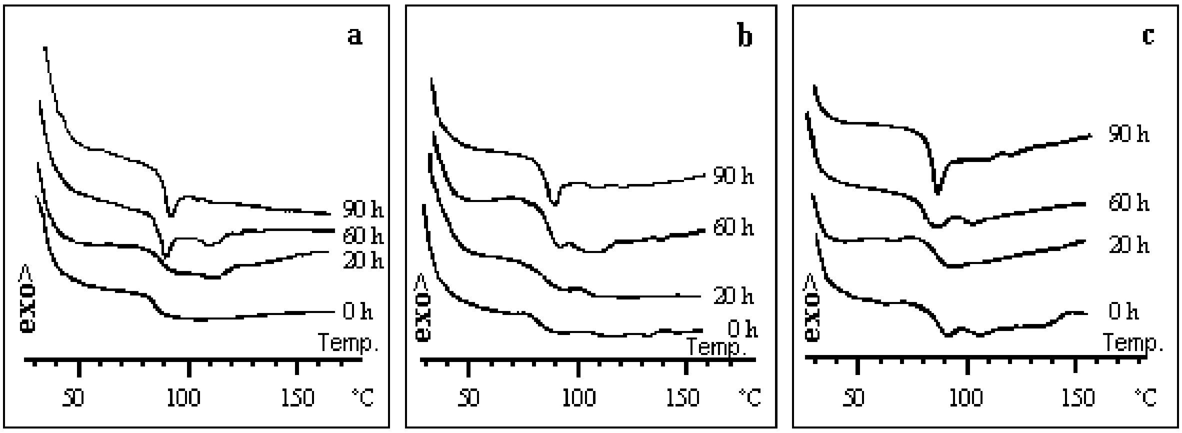


Figure 5. DSC curves in the Tg region for three ageing stages; a) PVC B, b) PVC D, c) PVC H

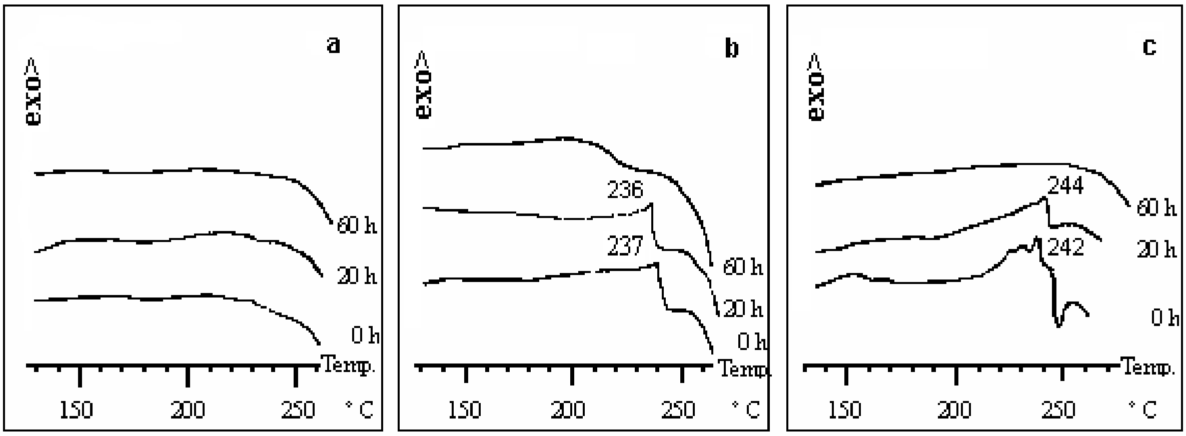


Figure 6. DSC curves in the temperature range (150-260°C) and for three ageing stages of a) PVC B, b) PVC D and c) PVC H.

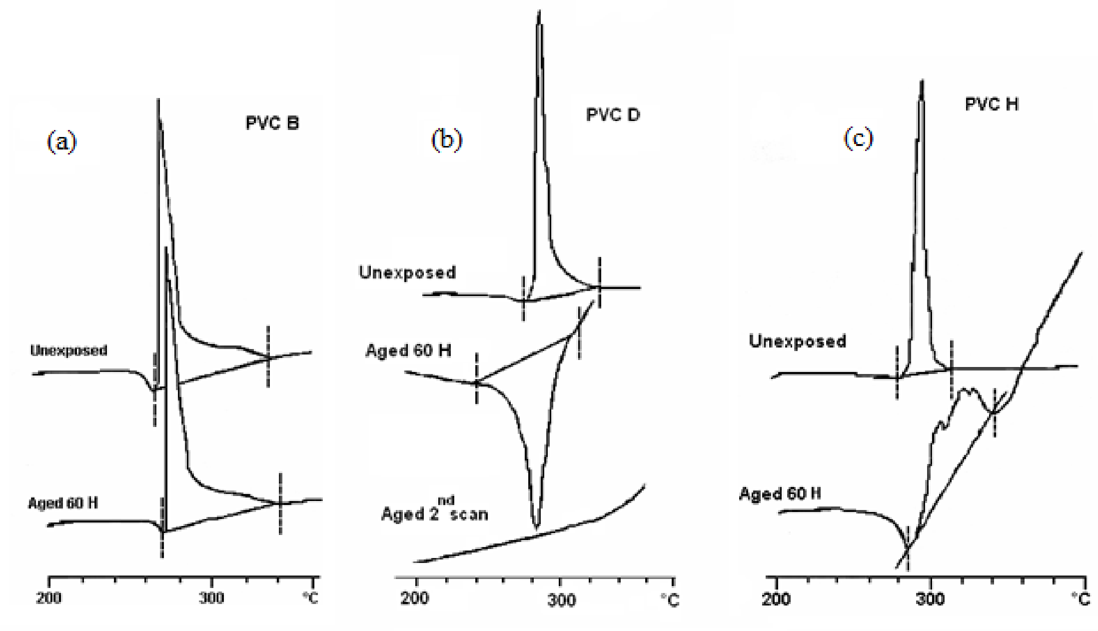


Figure 7. DSC curves in the range of temperature greater than 260°C of a) PVC B, b) PVC D, c) PVC H

In the case of PVC B photoageing does not modify the direction of the peak, it remains always exothermic.

For PVC D the peak is exothermic in the beginning and becomes endothermic with ageing. The endothermic peak lets suppose the existence of a crystalline phase and would correspond to its fusion if any. To verify this hypothesis the aged sample was cooled at the same rate than that of heating to allow a possible re-crystallisation. Afterwards, the sample was heated again under the same experimental conditions than those prevailing in the first scan. This time, the endothermic peak disappears completely indicating that it could most probably correspond to a dehydrochlorination process. For PVC H the peak is exothermic before ageing. Afterwards, for the aged stage, the thermogram shows an ambiguous behaviour which corresponds neither to an endotherm nor to an exotherm. An exothermic peak would have meant that oxidation is the dominant process compared to dehydrochlorination; the opposite would have been equaly true. In the case of PVC H, the two processes seem to be antagonist.

3.3 Oxidative Induction Time (OIT) measurements:

OIT measurements performed on the three formulations i.e. PVC B, D and H for three ageing stages are reported in table 3. For PVC D no OIT value has been recorded, the material oxidizes immediately after the change over point to air. For PVC B only one value has been recorded for the first ageing stage. This result consolidates the initial hypothesis that Ba/Cd/Zn has almost completely reacted during processing. It is only the remaining concentration after processing which ensured the thermal stability of the mixture and allowed this first and single point of measurement.

For the remaining ageing times, the sample is instantaneously oxidized at the change over point to air, because of the complete stabilizer consumption.

For PVC H, an OIT value has been recorded for all the ageing stages. Nevertheless, this oxidation time decreases progressively with exposure time.

Table 3. OIT measurements of PVC B and H for three ageing stages 20, 60 and 90 hours.

Exposure time (H)	**20**	**60**	**90**
PVC B	06’40’’	-	-
PVC H	17’00’’	16’07’’	13’00’’

This gives two important information, the first one is that DLS has not completely reacted during processing; the second one is that DLS interacts with light and it is progressively consumed with time.

3.4 Thermogravimetric analysis

The thermogravimetric analyses were performed on the same test pieces i.e. PVC B, D and H and for the same ageing stages. On figure 8 are reported their respective TG curves. An accurate observation of the TG curves of the three formulations at the first ageing stage reveals that dehydrochlorination starts earlier for PVC D, then it is followed by PVC H and PVC B respectively (Fig. 8a). This order remains unchanged for the aged films (Fig. 8b). To make easier the comparison between the thermal properties of each formulation all the significant greatnesses have been reported in tables 4 and 5. In the case of PVC B and PVC H the relative weight loss does not change significantly with exposure time since it varies from 57% to 58 % for the first and remains close to 59% for the second. For PVC D, the weight loss is more sensitive to the effect of ageing. In fact, it passes from 51% for the first ageing stage to 59% for the last one. In the three cases, the total duration of the dehydrochlorination process (t_T) slightly increases with exposure time, although this is more significant for PVC D.

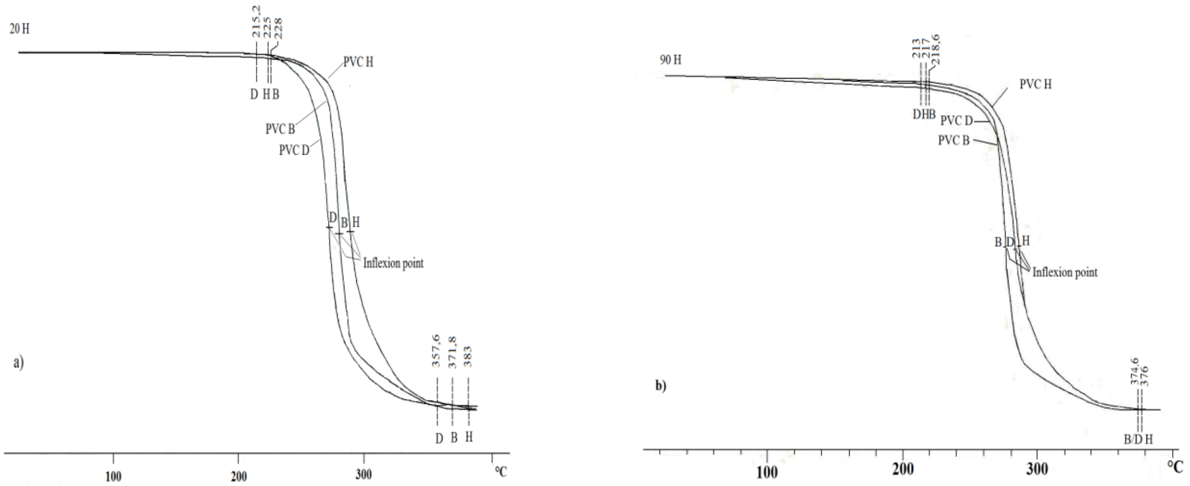


Figure 8. TG curves of PVC B, D and H a) 20 hours exposure b) 90 hours exposure.

Table 4. Relative weight loss (ΔM) and the total duration of the dehydrochlorination process (t_T) of PVC B, D and H.

Exposurtime (H)	**PVC B**		**PVC D**		**PVC H**	
	ΔM%	**t_{Tmn}**	**ΔM%**	**t_{Tmn}**	**ΔM%**	**t_{Tmn}**
20	57.32	14.57	51.42	14.23	59.68	15.59
60	57.31	14.75	58.29	16.44	59.40	16.10
90	58.44	15.59	59.70	16.77	59.08	16.10

Table 5. T_{peak} the half-life temperature (T_{50}) and its corresponding time (t_{50}) of PVC B, D and Hfor three ageing time.

Exposure time (H)	**PVC B**			**PVC D**			**PVC H**		
	T_{peak} (°C)	**T_{50} (°C)**	**t_{50} (mn).**	**T_{peak} (°C)**	**T_{50} (°C)**	**t_{50} (mn).**	**T_{peak} (°C)**	**T_{50} (°C)**	**t_{50} (mn).**
20	281.5	281.9	26’	272.5	273.1	24’49”	287.5	290.3	26’32”
60	278.5	278.7	25’22”	277	277.6	25’16”	292	293.3	26’50”
90	275.5	276.6	25’10”	284.5	285.7	26’	284.5	286.3	26’08”

T_{peak}, which occurs at the inflexion point of the TG curve and corresponds to the maximum rate of dehydrochlorination, varies differently from one mixture to another (Table 5). For PVC B it decreases with exposure time with a regular step of 3°C, (i.e. a total progress of 6°C). For PVC D T_{peak} varies in an irregular manner, but shows a global increase of 12°C. For PVC H, it varies in a non-monotonous manner and the last value is lower than the first of about 3°C.

The same variations have been observed for the half-life temperature (T_{50}) of the three mixtures. Moreover, the (T_{50}) values are very close to those of T_{peak}. This tends to confirm the evidence that the maximum of the DTG curve occurs when the product has almost lost the half of its original weight. This would also indicate that T_{50} and T_{peak} have nearly the same physical meaning.

4. DISCUSSION

Thermal analyses performed in this study have shown that this grade of PVC used to produce the films is highly amorphous. The DSC thermograms of the films present three distinguishable regions relevant to physical transitions and/or chemical reactions. The first transition, which appears on the thermogram, is the glass transition temperature, it occurs just above 80°C. The second one appears as a small endothermic peak just above 230°C and this only for PVC films stabilized with the lead based stabilizer. The last one occurs around 280°C; it can appear either as an endotherm or as an exotherm.

Ageing effects on unstabilized PVC:

The results presented above show that the ageing of PVC films with artificial UV light at a temperature of 70°C provokes significant microstructural changes and affect the thermal behavior of the material as well.

The first transition recorded for the unstabilized film is Tg which occurs at 89°C. The sensitivity of PVC towards heating has been verified via two successive scans and it appears that Tg slightly increases by a few degrees.The shift of Tg to higher values is related to structural changes induced by heating and the most likely reason seems to be crosslinking formation. The formation of primary bonds between the macromolecular chains reduces drastically the mobility between them, consequently the glass transition shifts to higher temperatures.

The second transition recordable in unstabilized PVC should normally be the fusion of the crystalline structure if any, and should normally appear around 280°C [20]. However, no fusion peak has been identified on the DSC thermogram of the virgin material. Instead, it occurs a broad exothermic peak belonging to an oxidation process. The test being performed under inert atmosphere this let us believe that this oxidation has been made possible thanks to oxygen molecules entrapped in the polymeric matrix during the films processing. If the test is performed under air instead of a broad exothermic peak of oxidation, it appears an endothermic peak. This occurs, despite the fact that the sample was surrounded by atmospheric oxygen.

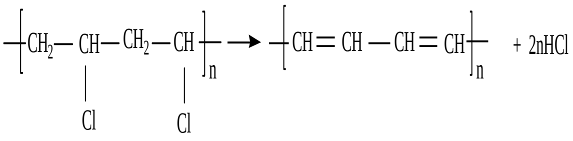
This singular behaviour can be explained by the fact that in the presence of atmospheric oxygen, the PVC thermal degradation is considerably accelerated and becomes more complex. The reaction of atmospheric oxygen with the polymeric chains takes place earlier and dehydrochlorination too. This leads to the formation of oxygen containing groups, initially hydroperoxydes which decompose by producing radicals that may attack the polymeric chains leading to secondary initiation of HCl loss and dehydrochlorination becomes considerably accelerated but progressive with the temperature rise [21]. Therefore, the endothermic peak can be regarded as the maximum rate of the dehydrochlorination process detectable by the apparatus in the limit of its sensitivity. The second scan performed on the same sample and in the same environmental conditions did not display this peak. This means well that i) it does not correspond to the fusion of a crystalline structure, otherwise PVC should have recrystallized during cooling and ii) that dehydrochlorination has probably been completed at the end of the first scan (Fig.1 a, b, c). The thermogravimetric results support these above hypotheses. In fact, heating of PVC provokes an irremediable dehydrochlorination process. This process becomes measurable and detectable on the TG thermograms at temperatures above 210°C (Fig. 2 and 8). In inert atmosphere or in air the inverted S-shaped curves of the TG thermogram shows well that dehydrochlorination is an autocatalytic process and in both cases the maximum rate occurs around 280°C. This temperature seems to be specific since it is common to TG and DSC and correspond independently either to oxidation, dehydrochlorination or to the fusion of crystalline structures if any.

In inert atmosphere the release of chlorine atoms is very close to the chlorine content of the polymer which is about 56% of its total weight. When the test is performed in air the weight loss is lower. This difference can be explained by the fact that in parallel to the HCl release, the surrounding oxygen reacts with the polymeric radicals formed either by chains cleavage or by hydrogen and/or chlorine atoms abstraction [22]. Therefore, these thermo-oxidation reactions reduce partially the total weight loss because of the addition of oxygen atoms to the polymeric chains.

The exposition of PVC film to UV light affects the physical properties of the material. Tg initially recorded at 89°C decreases from about 5°C. The total weight loss decreases and the variation between the weight loss recorded in air and the one recorded in inert atmosphere also diminishes.

These variations can be explained by the fact that in the material it occurs many chemical reactions and the most important among them are crosslinking and chain scissions which remain in competition for all the duration of the ageing protocol [4,10,12]. At an advanced ageing stage, chain scissions become predominant. Therefore, they lower the average molecular weight and decrease the glass transition temperature as well. During the photooxidation of the films a small amount of labile chlorides is eliminated, therefore the total amount of HCl released during the TG test becomes lower and the variation in weight loss between the two different experimental environments is also lowered.

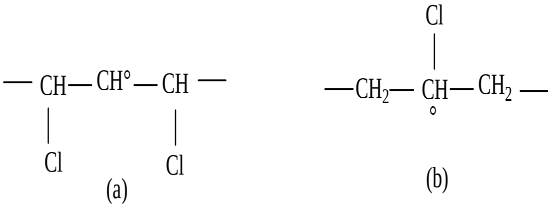
The degradation of PVC is known to cause the loss of hydrogen chlorides, initiated at the unstable sites. The cleavage of C-Cl bonds in allylic placements resulting from an intermolecular energy transfer can be reasonably supposed. This leads to the formation of long coloured polyene chains; a simplified mechanism is sketched in figure 9 [23].



$$\left[-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-\right]_n \rightarrow \left[-CH=CH-CH=CH-\right]_n + 2nHCl$$

Figure 9. Dehydrochlorination reaction, formation of polyene sequences and HCl release.

Obviously the actual mechanism is much more complex and involves the formation of radicals which themselves favour abstraction of hydrogen and chlorine atoms [24-27]. In PVC, hydrogen abstraction from methylene group (-CH_2-) is more probable than the abstraction of tertiary bonded hydrogen from a –CH(Cl)- group, due to polar effects [28]. However, the resulting two radicals are both produced and coexist during the ageing process (Fig. 10 a, b).

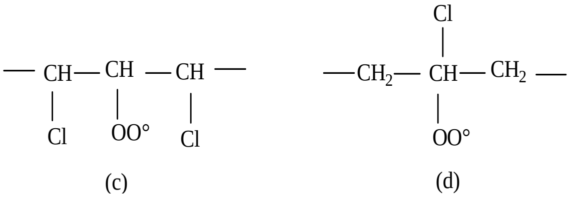


$$-\underset{Cl}{CH}-CH^{\circ}-\underset{Cl}{CH}- \qquad -CH_2-\overset{Cl}{\underset{\circ}{CH}}-CH_2-$$

(a) (b)

Figure 10. Alkyl radical formed by hydrogen abstraction

The reaction of these radicals with molecular oxygen leads to peroxy radicals (Fig.11 c, d).

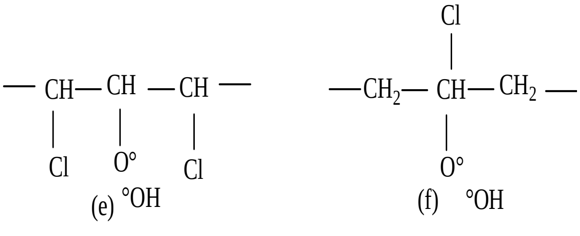


$$-\underset{Cl}{CH}-\underset{OO^{\circ}}{CH}-\underset{Cl}{CH}- \qquad -CH_2-\overset{Cl}{\underset{OO^{\circ}}{CH}}-CH_2-$$

(c) (d)

Figure 11. Peroxy radicals formed by addition of molecular oxygen

Hydroperoxydes are then formed; they can be detected by their IR absorption at 3300-3400 cm^{-1}. Both thermolytic and photolytic conditions favor the homolysis of the O-O bond of these hydroperoxydes (Fig.12 e, f).



$$-\underset{Cl}{CH}-\underset{O^{\circ}}{CH}-\underset{Cl}{CH}- \quad {}^{\circ}OH \qquad -CH_2-\overset{Cl}{\underset{O^{\circ}}{CH}}-CH_2- \quad {}^{\circ}OH$$

(e) (f)

Figure12. Formation of alkoxy radicals

The evolution of these alkoxy radicals leads to the formation of end products such as alcohols, α and α' chloroketones, acid chlorides or carboxylic acids (Fig.13). From this simplified mechanism it becomes clear that backbone scission and crosslinking occur simultaneously. In the presence of air, oxy and peroxy radicals may participate in crosslinking reaction by termination. In the core of the film, where oxygen is in lower concentration than that of the surface, crosslinking may be achieved via the termination reaction of two macroradicals. Therefore, bonding can occur between two alkyl radicals as described in figure 14 a [26, 28].

In some cases when dehydrochlorination becomes more effective the formation of double bonds is favored. A double bond can act as a site for subsequent rapid elimination of HCl and a conjugated polyene is then formed via the so-called unzipping reaction. The conjugated polyenes are extremely reactive and crosslink via a free radical mechanism [29, 30] (Fig.14 b).

The effect of the formation of polyenes is the yellowing of the films, if their concentration continue to increase then the samples become darker.

On a mechanical point of view PVC crosslinking is known to increase the elastic properties of the films which become less ductile. At an advanced ageing stage, chain scissions becoming more important than crosslinking the films which were ductile become brittle. Therefore, the role of the stabilizers is to prevent or to postpone the adverse effects of ageing on the material.

Ageing effects on stabilized PVC:

The addition of stabilizers to PVC modifies its thermal behaviour and affects the ageing process as well. It does not appear a simple relationship between the concentration of the respective stabilizers and their effects on Tg. However, for the same concentration of the mixture of Ba / Cd / Zn, Tg decreases slightly more than it does with DLS.

When the two stabilizers are mixed together in equal concentration Tg decreases more. So, the presence of a stabilization system can affect this temperature in two manners; i) during processing it lowers the occurrence of crosslinking which in the contrary tends to increase Tg, ii) the presence of metal soaps between the molecular chains reduces their polar interactions and so tends to reduce the number of secondary bonds.

Differential scanning calorimetry is sensitive to DLS. In the DSC thermogram a small exothermic maximum appears just above 220°C. This maximum increases in sharpness and shifts to higher temperatures with the increase of the DLS concentration (Fig. 3) [31]. The absence of such an exotherm for the film stabilized with the Ba/Cd/Zn mixture would reinforce the assumption established thanks to the FTIR results [12], that this stabilizer has almost completely reacted during processing.

The variation of Tg (Fig. 4) and the changing shape of the portion of the curve relative to this transition which becomes a small endothermic minimum (Fig. 5) indicate that the films are subjected to a physical ageing during UV exposure despite the presence of a stabilization system.

For PVC H, the decrease of Tg up to approximately the middle of the ageing protocol duration, followed by its increase until it reaches the initial value of the starting material, indicates that the stabilizer is consumed gradually throughout the ageing time (Fig. 4) [19]. The ageing temperature is slightly below the onset of the glass transition temperature (ca.70 ° C); therefore the films are subjected to a physical ageing which becomes more effective after the stabilizer consumption [13]. The more probable structural change, which can be the reason for the appearance of this small endothermic minimum, is crosslinking resulting from a photochemical process involving radical reactions (Fig.14).

The small exothermic peak, at temperatures above 220°C, which varies with the DLS concentration, brings useful information on the kinetic of the stabilizer consumption (Fig. 3). In fact, the effect of UV light on the stabilizer leads to the gradual disappearance of this small exothermic peak with exposure time (Fig. 6).

Therefore these above observations confirm our hypotheses that i) DLS does not react entirely during processing, ii) it interacts with UV light providing a stabilizing action by replacing labile chlorides by more stable structures (Fig.15), iii) the absence of any effect of (Ba / Cd / Zn) on the DSC thermogram supports the hypothesis that they have reacted almost completely during processing and this is in accordance with the reaction proposed in figure 16. Therefore, the primary role of PVC stabilizers is to absorb and neutralize HCl released during processing and/or during ageing to prevent further oxidation reactions and other free radical processes [32].

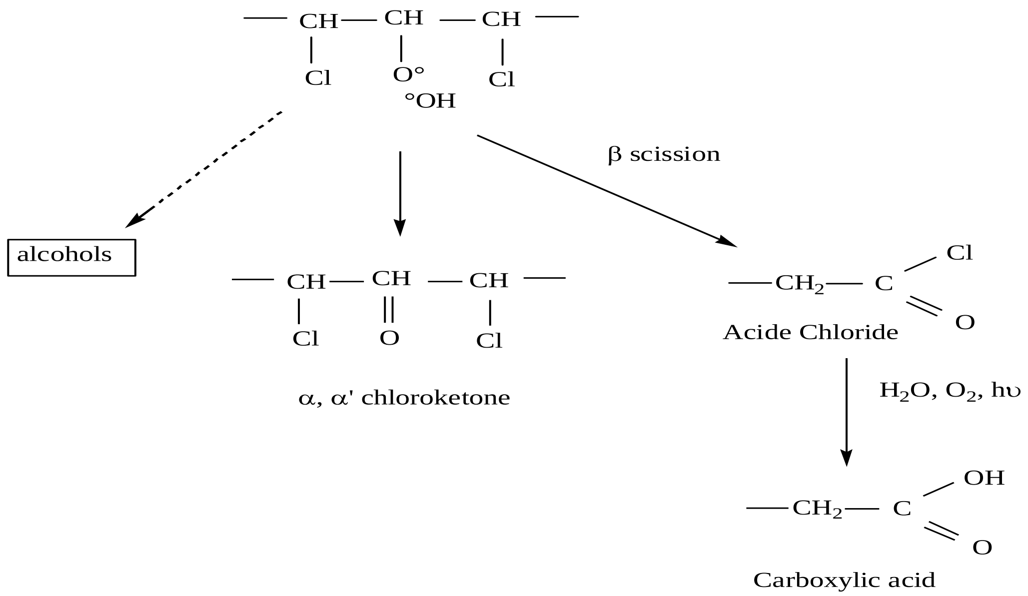


Figure 13. Formation of end products from the reaction of alkoxy radical

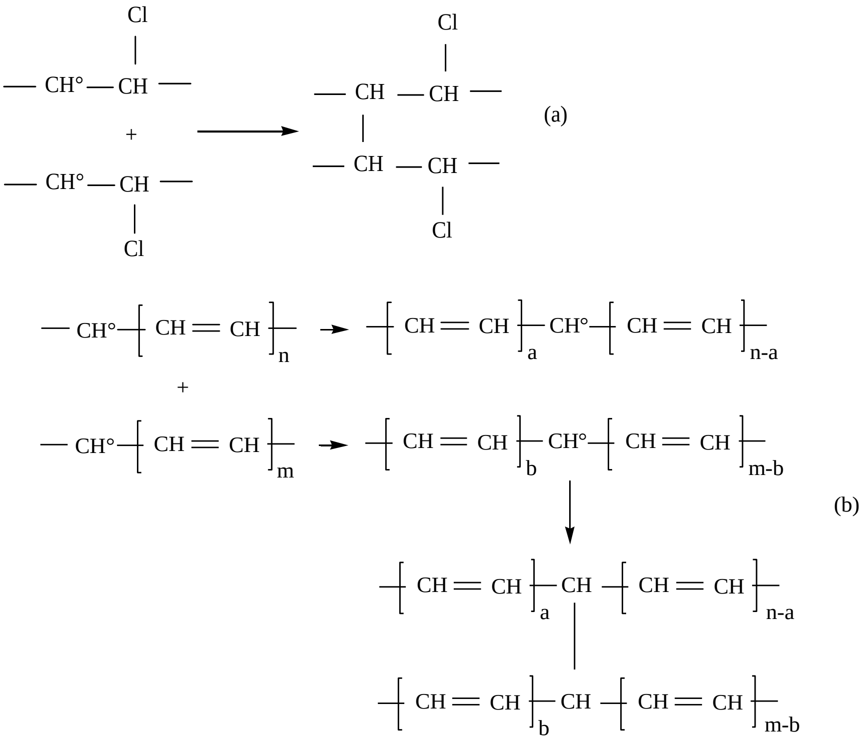
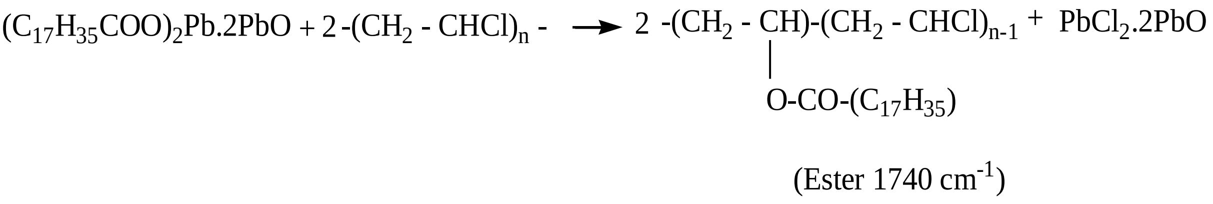


Figure 14. Crosslinking reactions a) between two alkyl radicals b) between two polyenyl radicals



$$(C_{17}H_{35}COO)_2Pb.2PbO + 2\,\text{-}(CH_2 - CHCl)_n\text{-} \longrightarrow 2\;\text{-}(CH_2 - \underset{\displaystyle O\text{-}CO\text{-}(C_{17}H_{35})}{\underset{|}{CH}})\text{-}(CH_2 - CHCl)_{n-1} + PbCl_2.2PbO$$

(Ester 1740 cm^{-1})

Figure 15. Basic mechanism of the chemical reaction of DLS with PVC.

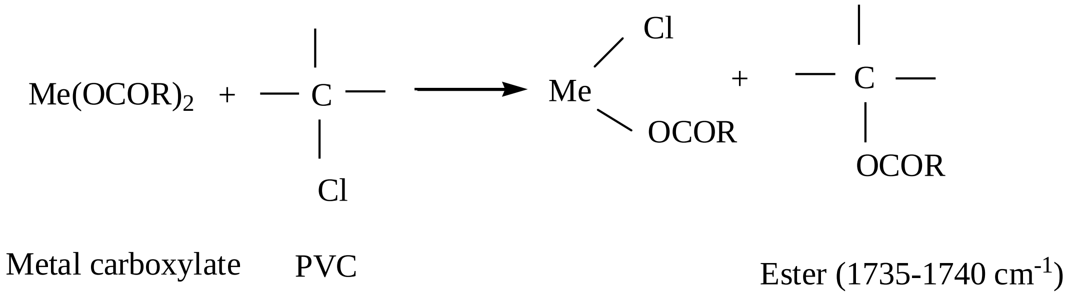


Figure 16. Reaction of the Ba/Cd/Zn carboxylate soap with PVC

Free and Horst [33, 34] found evidence for the introduction of ester groups in the polymer from metal carboxylate stabilizers. They postulate that thermal stabilizers function by substituting the unstable chlorine atoms, such as tertiary and allylic chlorine atoms, with the ligands of the stabilizer to yield derivatives, which are more stable than the original chloride and disrupt conjugations in the polymer chains to prevent objectional discoloration [33-37].

According to the thermal analysis results and what has been investigated elsewhere [12] it can be definitely postulated that the two stabilizers operate their stabilizing action differently.

The Ba/Cd/Zn mixture has nearly completely reacted during processing replacing most of the labile chlorides. The DSC thermograms of unexposed and aged PVC B show respectively two exothermic peaks at temperatures above 260°C indicating that its thermal behaviour is stable. Thus, this would indicate that PVC B does not undergo major structural changes.

DLS has partially reacted during processing and the remaining concentration interacts with UV light once exposed. The reactive part of the stabilizer provide structural changes to the material, this affects its thermal behaviour which leads to a peak inversion characteristic to a dehydrochlorination process for PVC D, or to an undefined behaviour for PVC H.

The effectiveness of the stabiliser systems has been performed by oxidative induction test. Only one value corresponding to the first ageing stage has been recorded for PVC B. For the remaining ageing time no value has been recorded. The first OIT value suggests that a very small amount of unreacted Ba/Cd/Zn remains after processing. The latter is however undetectable by FTIR or by DSC, probably because this concentration is too low and below the sensitivity limit of the apparatuses.

On the other hand, PVC H shows better performance to withstand heat effects. The progressive decrease of OIT with exposure time reveals the interaction between UV light and the stabilizer. This latter is progressively consumed with exposure time. Therefore, it can be postulated that DLS has effectively only partially reacted during processing and it is the remaining concentration, which allows the three OIT measurements.

Thermogravimetric analysis has revealed that the weight loss of stabilized PVC H is higher than that of the unstabilized. The weight loss of the first is 59.68% while that of the second is 55.57%. This last value is close to the chlorine content of PVC (i.e. 56 %).

The main reason for this difference is obviously the presence of the stabilizer and the manner with which it performs its stabilizing action. In fact, DLS provides two different effects i) it replaces labile chlorides by more stable structures and ii) it scavenges HCl to avoid a zipper like dehydrochlorination process. In figure 15, it appears that lead atoms, which produce the molecules $PbCl_2PbO$, trap the chlorine atoms. Therefore, it can easily be supposed that during testing, once the temperature becomes high enough, a given amount of these molecules is released along with those of the hydrochloric acids. This has the effect of considerably increasing the total amount of material released.

5. CONCLUSION

In this study, it has been reported that differential scanning calorimetry and thermogravimetry are two powerful tools providing useful information in understanding the mechanism of photodegradation of virgin and stabilized PVC.

Ba/Cd/Zn and DLS are thermal stabilizers used in the Algerian plastic pipes industry. They make possible the extrusion of PVC at an adequate processing temperature and they prevent earlier thermal degradation of the material. It has been shown that these two heat stabilizers provide also a good light stability.

On a morphological point of view, addition of stabilizers to PVC lowers its glass transition temperature either by preventing formation of crosslinking during processing or by reducing the number of secondary bonds between the molecular chains.

DSC is sensitive to the presence of DLS. Its presence provokes the appearance of a small exotherm above 230°C whose sharpness is proportional to the stabilizer concentration. This make it possible to follow the consumption of the stabilizer with ageing time.

The OIT measurements revealed that it remains a small amount of unreacted Ba/Cd/Zn. This was detected neither by IR spectroscopy nor by DSC. This technique has also been found very efficient to follow the progressive consumption of DLS, revealing as such the interaction of UV light on DLS. The combination of the two stabilizers did not give conclusive results in term of synergism.

Finally, it can be concluded that i) the thermal analyses have validated previous hypotheses [12] ii) and thanks to these results it can be definitely advanced that the two stabilizers operate their stabilizing action differently.

It can be considered that DLS acts in two steps:

- A first fraction of the stabilizer is consumed during processing. It scavenges HCl and prevents thereby unzipping process; it replaces labile chloride by more stable structure. This provides a greater thermal stability to the material.

- Once exposed to light the remaining fraction of DLS interacts with UV radiation and prevents a dehydrochlorination process. The stearic part of the stabilizer replaces labile chloride by a more stable structure with a longer-term stability.

In the case of Ba/Cd/Zn metal salts carboxylate, they react almost completely during processing by replacing tertiary and allylic chlorides (via the Free-Horst mechanism) leading to a PVC structure with a longer-term stability. At the post processing-stage, it remains a very small concentration of unreacted stabilizer, which as DLS interacts with UV light providing a stabilizing action. The final molecular structure, resulting from all the chemical reactions of stabilisation, becomes more stable and less sensitive to the deleterious effect of UV light.

The combination of the two stabilizers at various concentrations has lead to a variety of behaviour. However, on a chemical or on a thermal point of view no specific synergistic effect has been identified. At this stage of our investigations, it remains difficult to definitely conclude that none of the proposed formulations leads or not to an improvement of the PVC stability. Additional tests such as UV, NMR spectrometry or mechanical testing would have provided additional information making possible to reveal any possible synergistic combination.

Finally, it can also be advised that an analysis by means of a detector of the outgoing gases evolved during the pyrolysis of the films would also give a good insight on the effectiveness of the stabilizing system of the different mixtures. In fact, beside the evolved HCl during the temperature rise in the TG test some metal residues coming from the stabilizers could highlight on the chemical reaction involved in the stabilisation mechanism.

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