

Effect of thermal stabilizers (Ba/Cd/Zn metal salts carboxylate and dibasic lead stearate) on the kinetic of carbonyls formation of PVC films

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أجرينا هذه الدراسة على رقائق الـ PVC المستقرة والغير مستقرة، هذا النوع من الخليط معد لنقل المياه في المناطق الشبه صحراوية والجافة. حضرت ثمانية أنواع من الأمزجة باستعمال مثبتين في مختلف التراكيز. المثبتان المستعملين هما كربوكسيلات Ba/Cd/Zn وثنائي قاعدة الرصاص (DLS). التحاليل الطيفية باستعمال الأشعة ما فوق الحمراء تظهر أن خلال عملية التحول (لتحضير الرقائق) أن أملاح الكربوكسيلات Ba/Cd/Zn تتفاعل بشكل شبه تام مع PVC إلا أن (DLS) له تفاعل جزئي فقط. إن تعريض الرقائق لأشعة تحت البنفسجية يؤدي إلى تشكل نواتج مؤكسدة مثل الهيدروبيروكسيد والكربونيل والنواتج مزدوجة الروابط. كما أن وجود المثبت في الـ PVC يغير حركية ونوع الناتج المؤكسد المشكل. وكمثال في حالة (DLS) نلاحظ أن التراكيز الباقية من عملية التحول قد استهلكت عند التعريض إلى أشعة تحت البنفسجية UV تماما. و هذا يؤدي إلى تشكل ملحوظ في حمض الكربوكسيليك و تركيزه الخاص بنهاية التفاعل غير أن في حالة Ba/Cd/Zn سرعة تشكل تجمعات الكربونيل تناقصت بصفة معتبرة و كذلك الحال بالنسبة إلى تركيز نهاية التفاعل.

مثبتات حرارية تحليل طيف IR.

الكلمات المفتاحية: PVC

Résumé

Cette étude a été conduite sur des films non stabilisés et stabilisés de PVC vieilli au moyen d'une lumière UV artificielle. Ce type de mélange rentre dans la fabrication de tuyaux en PVC destiné aux transports de l'eau d'irrigation dans les zones arides subsaharienne. Huit (8) mélanges de PVC ont été préparés en introduisant deux types de stabilisants à diverses concentrations. Les deux stabilisants utilisés sont respectivement le carboxylate de Ba/Cd/Zn et le stéarate dibasique de plomb (DLS). L'analyse spectroscopique Infrarouge montre que pendant le processus de transformation (pour produire les films), les sels de carboxylate de Ba/Cd/Zn réagissent presque totalement avec le PVC alors que le stéarate dibasique de plomb (DLS) réagit seulement partiellement. L'exposition des films à la lumière UV conduit à la formation de produits d'oxydation tels que les hydroperoxydes, les carbonyles, et les insaturations. La présence de stabilisants dans le PVC modifie la cinétique et le type de produit d'oxydation formé. Par, exemple dans le cas du DLS on a observé que la concentration restante postérieurement au processus de transformation est finalement consommée pendant l'exposition aux UV. Ceci augmente considérablement le taux de formation de l'acide carboxylique et sa concentration de fin. Par contre dans le cas du Ba/Cd/Zn la vitesse de formation des groupements carbonyles est considérablement réduite et leur concentration de fin est également diminuée.

Mots clés : PVC; Photodégradation; Oxydation; Stabilisants thermique; spectroscopie IR.

Abstract

The study of the photodegradation of unstabilized and stabilized PVC films has been performed by means of artificial UV light. Eight (8) mixtures of PVC have been prepared by compounding PVC powder with two kinds of stabilizers at varied concentrations. The two stabilizers used are namely Ba/Cd/Zn carboxylate and dibasic lead stearate (DLS). The IR spectroscopic analysis has shown that during processing (to produce the films), the Ba/Cd/Zn carboxylate salt reacts almost completely with PVC while the dibasic lead stearate (DLS) reacts only partially. The exposition of the films to UV light leads to the formation of oxidation photoproducts such as hydroperoxides, carbonyles, and unsaturations. The addition of stabilizers to PVC has modified the kinetic and the kind of the oxidation products. For, example in the case of DLS it has been observed that the remaining concentration of this stabilizer after processing is consumed during UV exposure and it considerably increases the rate of carboxylic acids formation and their end concentration. In the case of Ba/Cd/Zn, the rate of carbonyl groups formation is slowed and their end concentration is lowered too.

Key words: PVC, Photodegradation, Oxidation, Heat stabilizer, IR spectroscopy.

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1. INTRODUCTION

The processing of PVC without heat stabilizers leads to an irremediable degradation of the material. To avoid this disagreement and to help processing, factories producing PVC tubes and pipes add into the PVC recipe heat stabilizers. This avoids to the material an excessive dehydrochlorination leading to a rapid burning of PVC into the processing tool. Most of the industrial stabilizers prevent material degradation by replacing labile chlorines with much more stable substitutes.

PVC tubes ensuring water transportation to agricultural lands in the Sahara are subjected to the very intensive and deleterious effect of solar light. The ultraviolet range of solar light is known to be very energetic and thus responsible of the degradation of the most industrial polymers. This ultimately leads to an undesirable loss of the mechanical and the surface properties.

The reasons of the high photosensitivity of PVC toward UV light is still not completely elucidated, since the monomer unit itself constituted of saturated bonds do not contain chromophores absorbing in the solar emission range. Commonly, polymer degradation is supposed to start from structural defects of the chains but their precise nature remains sometimes controversial or contradictory. Hydroperoxydes, carbonyls, unsaturations, residual metal salts (from catalyst) and structural irregularities (tertiary chloride, methine carbon of branching etc...) have been advanced as possible initiating chromophores [1-6].

Exposure of PVC films to UV light ($\lambda > 300\text{nm}$) provokes the formation of polyene sequences $-(\text{CH}=\text{CH})_n-\text{CHCl}-$ via dehydrochlorination reactions (zip dehydrochlorination) with concomitant evolution of HCl (fig. 1). Those

polyene sequences are photo-oxidizable and they quickly disappear on irradiation in the presence of oxygen [7, 8].

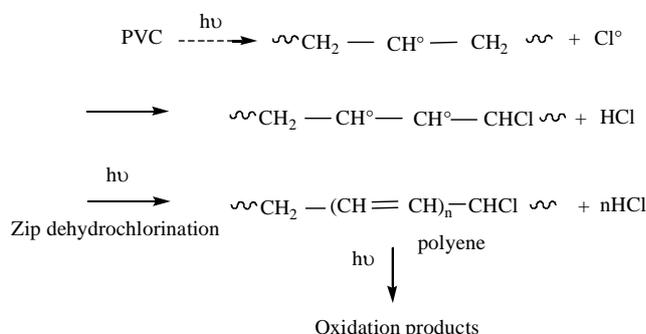


Figure 1. Zip dehydrochlorination mechanism.

The abstraction of labile chlorine atoms from the polymeric chains leads to the formation of radicals, which can themselves react with surrounding oxygen. The resulting peroxy radical react with a polymeric chain to form a hydroperoxyde, this last one can undergo a homolysis of the O-O bond under photochemical excitation. The cleavage of this bond gives an alkoxy radical. The evolution of this radical leads to several photo-oxidation products, that can be detected by their IR absorptions [7-9]. This is described through a simplified photo-oxidation mechanism sketched in (fig. 2).

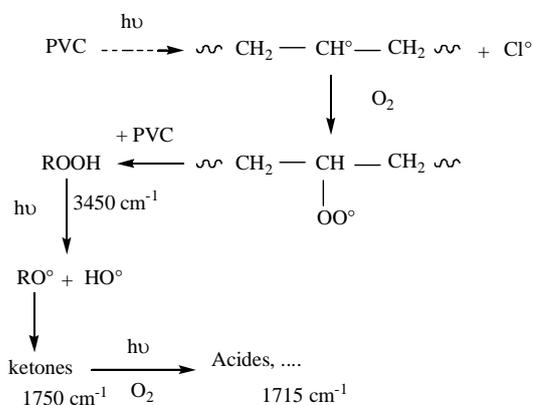


Figure 2. Simplified mechanism of PVC photo-oxidation.

On the IR spectrum appears a complex growing absorption band centered around

1730 cm^{-1} . Of course several groups involve the presence of a carbonyl group, which contribute to the broad band around 1730 cm^{-1} by shoulders which are difficult to analyze separately. The most common oxidation products which were identified in our study are listed below [3, 7-9]:

-1715-1718 cm^{-1} : Carboxylic acids

-1725-1745 cm^{-1} : α and β chloroketones

-1735 cm^{-1} : Ester groups

-1744-1750 cm^{-1} α and α' dichloroketones

For very long time of exposure, the band becomes very large and extends from 1680 to 1800 cm^{-1} . Other shoulders emerge on its both sides. These shoulders are other oxidation photoproducts, among them [3, 7]:

-1760- 1790 cm^{-1} : Acid chlorides, peracids, preesters and lactones.

-1680 cm^{-1} : Unsaturated ketones.

The addition of DLS to PVC gives a rise to a broad band at 1510-1540 cm^{-1} and at 1735 cm^{-1} . Those absorption bands can be assigned to the C=O valence of the incorporated lead salt [10-14].

This work shows how two stabilizers primarily used in the

Algerian industry of plastic to prevent PVC degradation during processing can affect the rate of formation and the end concentration of the oxidation photoproducts. The mixing of these two kinds of stabilizers, even with small variations of their respective concentration, can affect dramatically the oxidation kinetic.

Most of the works that deal on PVC photodegradation have been conducted on samples made by casting; such a method does not take into account the thermal history necessary in the industrial processing of PVC. For this reason, we chose to make films thanks to a method, which offers operating conditions as close as possible to those prevailing in industry.

PVC being very sensitive toward UV light it is expected that the most important oxidative reactions take place during the first hours of U.V exposure. It is for this reason that we have focused most of our attention on this critical period.

2. EXPERIMENTAL

Commercial PVC powder, supplied by the national society "ENIP" of Skikda, has been manually mixed with two kinds of stabilizers namely Ba/Cd/Zn carboxylate and dibasic lead stearate. This was done according to eight different formulations as indicated in table 1.

Table 1. The PVC formulations (concentration 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 |

The general chemical structure of the two stabilizers used is for:

DLS: $(\text{C}_{17}\text{H}_{35}\text{COO})_2 \text{Pb} \cdot 2\text{PbO}$
Ba/Cd/Zn carboxylate: MeOCOR

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 $^{\circ}\text{C}$.

To help the processing of the films and to ensure an external lubrication 1 phr (part per hundred resins) of LDPE has been added to all the formulations. It was checked that the presence of a small amount of LDPE does not affect the IR spectrum of PVC.

The formulations A, B and H were prepared to show the separated effect of each stabilizer and to allow a simple comparison. The others are combinations of the two stabilizers mixed at various concentrations. They make it possible to check if their combination at the concentrations studied can lead or not to a synergistic system.

To achieve the aging, the films were exposed to artificial UV irradiation at a temperature of 70 $^{\circ}\text{C}$. 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).

The apparition and the growth of new chemical species have been monitored by IR spectroscopy. The apparatus is a dispersive spectrophotometer Perkin Elmer 683 interfaced to a computer. Every ten hours of exposure a sampling of each formulation was done, this has been continued up to 70 H.

The specific absorption peaks were analyzed from the spectra delivered by the equipment. For each peak the "optical density" (OD) was determined following the usual definition as: $\text{OD} = \ln(I_0/I)$, where I_0 is the reference infrared intensity

corresponding to the baseline of the spectrum at the peak wave number and I is the minimum intensity at the base of the peak.

3. RESULTS AND DISCUSSION

Just after processing, the oxidation state of the films has been checked by IR spectroscopy. In all the cases, the films show an absorption band in the carbonyl region. This band increases from A (Unstabilized) to B, through D, C, E, F, H and G respectively.

Their respective carbonyl bands are constituted by the variety of oxidation photoproducts described in the introduction.

During exposure, the absorption band of the carbonyl groups of all the mixtures increases and widened to extend from 1680 cm^{-1} to 1800 cm^{-1} , with many shoulders on its both sides (fig. 3,4,5).

The IR spectral changes in the carboxylate region (1500-1600 cm^{-1}) were checked for all the mixtures. However, the absorption band around 1510-1540 cm^{-1} was only observable on the spectrum of mixtures containing DLS. The presence of this specific absorption is probably due to the vibration of the COO^- structure present in the stabilizer [10-12].

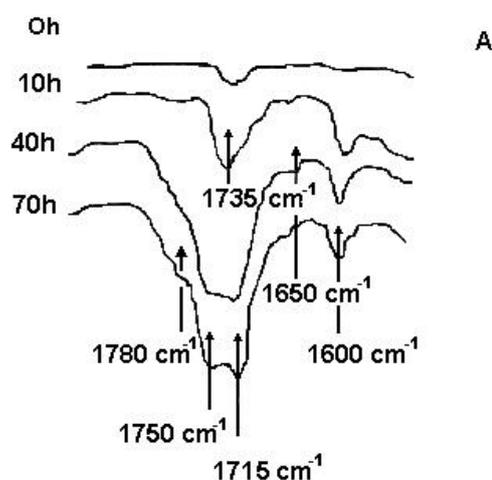


Figure 3. IR spectra [PVC (A), (Unstabilized)] for three aging stages (carbonyls region).

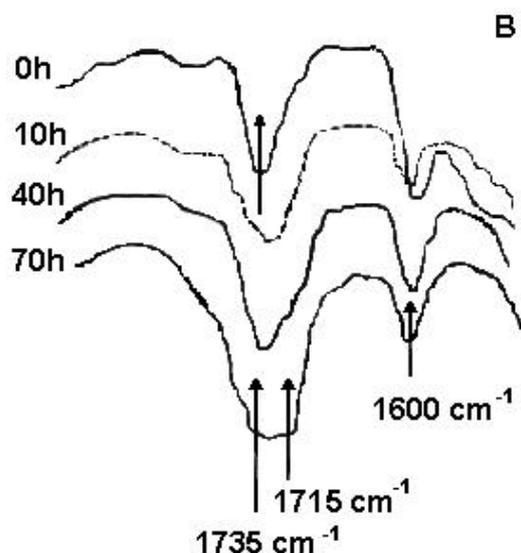


Figure 4. IR spectra of stabilized [PVC B, (Ba/Cd/Zn)] for three aging stages (carbonyls region).

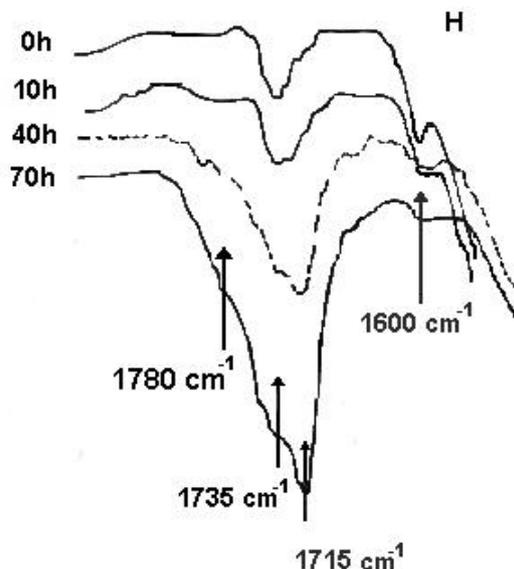


Figure 5. IR spectra of stabilized [PVC H, DLS] for three aging stages (carbonyls region).

A comparison of the carbonyl band of PVC A, B and H for three aging stages (fig. 3, 4 and 5), allows a simple comparison of each stabilizer effects on the kind and on the concentration of the oxidation products formed before and after aging.

3.1 Effects of the respective stabilizers on the type of oxidation products formed.

In this section an analysis and a comparison of the IR band of the three basic formulations i.e. (A, B, H) is carried out. Such an approach allows a qualitative evaluation of the effects of the respective stabilizers on the type of oxidation products formed.

Unstabilised PVC A makes it possible to highlight the influence of the two respective stabilizers on the oxidation mechanism.

On its spectrum, at zero time it appears only a weak carbonyl absorption band. After ten (10) hours of UV irradiation the carbonyl band increases and points at 1735 cm^{-1} and another absorption band at 1600 cm^{-1} generally ascribed to unsaturations appears too [7,15,16]. After 40 hours, the carbonyl band widens and its bottom flattens. As the oxidation progresses, it continues to widen and develops two maxima of comparable intensity, one at 1715 cm^{-1} and the other at 1750 cm^{-1} respectively, a shoulder at 1780 cm^{-1} is also observable.

At zero time PVC B (fig. 4) stabilized with Ba/Cd/Zn is more oxidized than PVC A. Its carbonyl band points intensively at 1735 cm^{-1} and the absorption at 1600 cm^{-1} is already well developed. Until 40 hours, the absorption band of carbonyls continues to point at 1735 cm^{-1} and the absorption band at 1600 cm^{-1} increases too. This last one remains present during all the UV treatment. At the last stage of aging, the concentration of the carboxylic acids (1715 cm^{-1}) reaches that of the esters (1735 cm^{-1}). The signal at 1780 cm^{-1} visible at zero hour becomes only a shoulder at 40 hours. Then it is no more observable because its signal is completely overlapped by the carbonyl's band, which became broader.

At zero time, PVC H (fig. 5) points less intensively at 1735 cm^{-1} than it does in PVC B. The absorption band at 1600 cm^{-1}

is also less significant and disappears at an early stage of exposure.

The growth of the carbonyl band is different to that of the two other mixtures. At the beginning of the exposure, the carbonyl's rate formation is very low. After forty hours, it starts a very rapid increase and the absorption band points intensively at 1715 cm^{-1} . At the end of the exposure, on the massive absorption band, the esters at 1735 cm^{-1} appear only as a shoulder while carboxylic acids show a much higher concentration.

3.2 Effect of respective stabilizers on carbonyl formation kinetics

The graphical representation of the variation of the optical density (O.D) measured at the maxima of the carbonyl bands of the three basic formulations (A,B,H) versus exposure time are reported on (fig. 6). This allows a simple but a quantitative comparison of the carbonyl groups formation's kinetic of the three respective formulations.

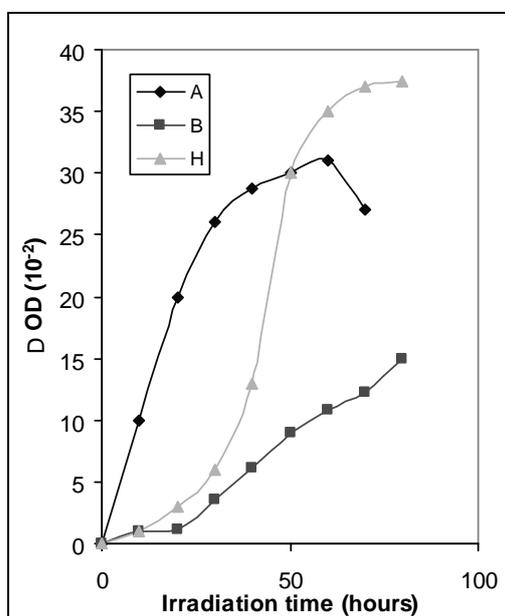


Figure 6. Relative optical density at 1715 cm^{-1} vs exposure time, PVC A, B and H, effect of the respective stabilizers on the oxidation kinetic.

Unstabilized PVC A knows an autoaccelerated carbonyl formation already at the beginning of the UV treatment. The rate of carbonyl groups formation is almost linear during the first thirty hours, just after it slows down and then saturates. Finally, it becomes negative beyond 60 hours of exposure.

Compared to the other mixtures PVC A (fig.6, 7 and 8) has the highest rate of carbonyl groups formation but it does not have the highest end concentration.

PVC B to which Ba/Cd/Zn has been added alone shows the slowest rate of carbonyl groups formation and has the lowest end concentration as well.

In PVC H where DLS is added alone, the carbonyl group's rate of formation is also reduced during the firsts thirty hours, but less than in PVC B. Beyond this limit of time the rate of carbonyl formation becomes auto-accelerated until 60 hours of exposure. During this period, the rate of formation reaches almost the infinity. Afterward, it slows down and saturates. The kinetic of the carbonyl groups formation follows an s-shaped curve. Finally, it can be noticed that the end's carbonyl groups concentration in PVC H is the highest compared to the two others.

3.3 Effect of DLS concentration, on the kinetic of the carbonyl groups formation (when added to one phr of Ba/Cd/Zn).

In the precedent section, the individual effect of each stabilizer on the oxidation kinetic was described. But, how does the kinetic or the end carbonyl groups concentration is affected by the progressive addition of one stabilizer to a fixed concentration of the other is discussed in this section.

The variations of the carbonyl groups formation and their end concentrations of formulations where DLS (from 0 to 2 Phr) was added to 1 Phr of Ba/Cd/Zn are reported in (fig. 7).

It has been found that the carbonyl groups end concentration and their rate of formation increase with the increase of DLS concentration. DLS seems to act as an auto-accelerator promoting the formation of oxidation products. To achieve this analysis the reverse was tried and this time Ba/Cd/Zn was added to DLS.

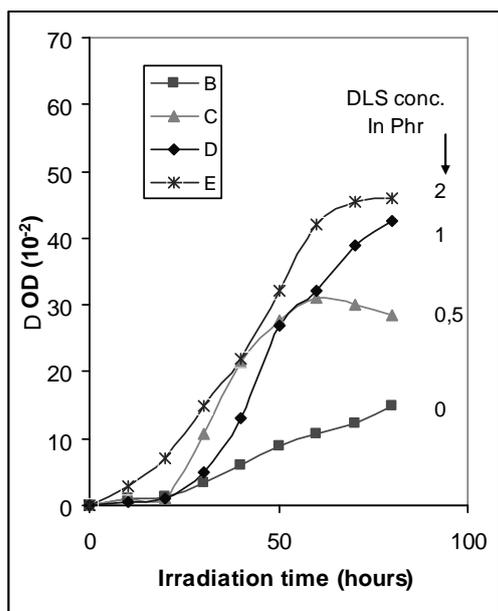


Figure 7. Relative optical density at 1715 cm^{-1} vs. exposure time (effect of DLS added to 1Phr of Ba/Cd/Zn).

3.4 Effect of Ba/Cd/Zn concentration, on the kinetic of the carbonyl groups formation (when added to one phr of DLS).

This section describes the effect of a progressive addition of Ba/Cd/Zn (from 0 to 2 Phr) to 1Phr of DLS on the kinetic of the carbonyl groups formation. The variation of the optical density versus exposure time of these different mixtures is reported on (fig. 8). It can be observed that the progressive increase of the Ba/Cd/Zn concentration lowers the carbonyl groups end concentration and their rate of formation as well. For a concentration of Ba/Cd/Zn equal to that of DLS (PVC D), the formation of oxidation

products is almost completely inhibited during the first 20 hours. Then it becomes auto-accelerated.

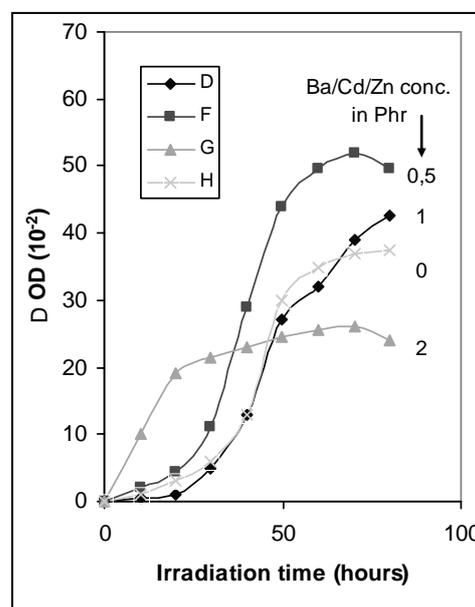


Figure 8. Relative optical density at 1715 cm^{-1} vs. exposure time (effect of Ba/Cd/Zn added to 1Phr of DLS).

A lower concentration of Ba/Cd/Zn (PVC F) has drastically increased the carbonyl groups end concentration and their kinetic of formation is auto-accelerated after a short induction period of about 20 hours. In a general manner, it can be considered that the addition of DLS with a higher concentration makes the kinetic of oxidation following an s-shaped curve.

3.5 Stabilizers Consumption

Addition of DLS to PVC gives rise to a peak around (1510-1540 cm^{-1}). This absorption band is specific to the presence of a stearate structure. This peak does not appear in the case of Ba/Cd/Zn carboxylate salts.

Combination of these two stabilizers with various concentrations affects the initial intensity of this peak of absorption and its speed of disappearance.

On (fig. 9) is reported the variation of this peak versus exposure time for five (5)

A transverse comparison of figures 7, 8, 9 shows that in the case of the formulations having an oxidation kinetic following an s-shaped curve, the kinetic curves of the stabilizer consumption follows an inverted s-shaped curve. In some cases as in PVC H the total consumption of the stabilizer coincide with the auto-accelerated formation of carboxylic acids.

In other studies, it has been shown that carboxylic acids formation is coming from the hydrolysis of acid chlorides themselves resulting from the β -scission of alkoxy radicals (fig. 10) consequently this leads to a decrease of the average molecular weight [7,8]. This is known to affect adversely the mechanical properties by lowering the properties at rupture.

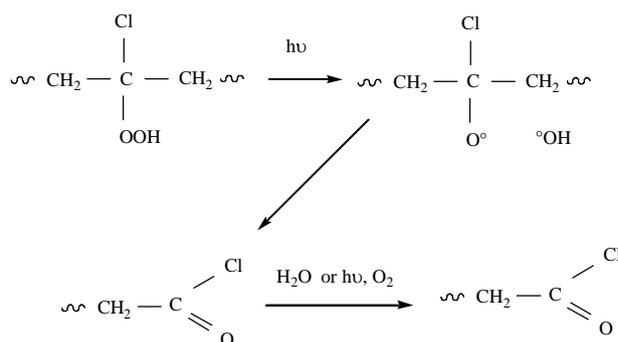


Figure 10. Chemical formation of carboxylic acid.

Addition of stabilizers can reduce (as in the case of Ba/Cd/Zn) or increase (as in the case of DLS) the carboxylic acid concentration.

In our case, it remains difficult to assess whether the carboxylic groups in stabilized systems come from chain scission reactions, or they are simply related to the reaction of the stabilizer with PVC.

However, the simplest way to check this assumption would have been to test the films mechanically since the properties at break are directly related to the molecular weight of the polymer. Of

course, it would have been very interesting to verify the potential relationship existing between the growths of the carboxylic acids and the evolution of the mechanical properties at rupture. Unfortunately, the technique used to prepare the films did not allow the fabrication of normalized test pieces for mechanical testing.

CONCLUSION

The poor thermal stability of PVC requires its processing in the presence of heat stabilizers. However, their addition to PVC modifies the mechanism of photooxidation. The rate, the kind and the total amount of photooxidation products are singularly affected.

The analyses have shown that Ba/Cd/Zn and DLS operate their stabilizing action differently.

- The first reacts almost completely with the weakest sites during processing. It replaces labile chlorines by carboxylate groups leading to a more stable PVC structure. Therefore, the new structure is not only more thermally stable but also less photosensitive. This is argued by the fact that no absorption band corresponding to the unreacted carboxylate part of this stabilizer appears on the IR spectrum of processed PVC B. Secondly, at this stage of the treatment ester groups (1735 cm^{-1}) are well developed consequently to the replacement of the labile chlorines by carboxylate substitutes.

- DLS does not react entirely during processing. The unreacted portion of the stabilizer shows an absorption band in the carboxylate region of the IR spectrum at ($1510\text{-}1540 \text{ cm}^{-1}$). During the UV treatment, this last one decreases progressively with exposure time consequently to the reaction of the stearic part of this stabilizer with PVC, by replacing labile chlorines by a more stable

structures. This gives rise to esters groups. The kinetic of the carbonyl groups formation in the presence of DLS follows an s-shaped curve. Their auto-accelerated formation coincides with the sudden consumption of the stabilizer. The total stabilizer consumption is accompanied by a drastic increase of the carboxylic acids formation. Carboxylic acids are known to be end products arising from chain scissions. However, they could also come from the reaction of the stabilizer with PVC producing carboxylic acid without any specific incidence on the average molecular weight. The simple way to verify this hypothesis would have been to test mechanically the films.

Mixing of the two stabilizers at various concentrations has led to a variety of behaviours, but no specific synergistic effect has been found. Contrarily to what it was expected, the addition of DLS to a lower concentration to that of Ba/Cd/Zn has significantly enhanced the carboxylic acid concentration, while the inverse has lowered it.

However, from all the proposed mixtures, the best stabilization system in terms of lowering the carbonyl groups concentration is Ba/Cd/Zn when added alone.

Addition of heat stabilizers to PVC leads to their reaction with the polymeric chains during processing and during exposure to UV light. This is followed by a modification of its chemical structure. However, what is their impact on the morphology and the thermal behaviour of PVC? this will be discussed in a forthcoming communication.

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