

# Stabilization of Poly(vinyl chloride) with Preheated Metal Stearates and Costabilizers. I. Use of a $\beta$ -Diketone

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**ABSTRACT:** The influence of a  $\beta$ -diketone on the already observed anomalous behavior of preheated metal stearates as stabilizers for PVC has been evaluated. During normal stabilization procedure, the addition of diketones reduce the stabilization times, but the pretreatment of the mixture of metal soaps or of the individual zinc soap (then added to the calcium soap) delayed such times, recovering to some extent the reduction induced by the costabilizer. The calcium soap preheated (added along with zinc stearate to PVC), on the other hand, reduced the induction times further. These findings obtained by measurement of induction times by means of loss of weight (TGA) and HCl evolution, have been supported by FTIR and visible reflectance studies. While using preheated ZnSt<sub>2</sub>, a second rate of dehydrochlorination was observed in the HCl evolution traces, suggesting a separate consumption of the compounds during the stabilization mechanism. In general, it can be said that preheated primary stabilizers and costabilizers have no significant interactions between them. The final result is just the addition of their separate effects. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1–10, 1998

**Key words:**  $\beta$ -diketone; preheated metal stearates; stabilization procedure

## INTRODUCTION

The mechanism of the thermal degradation of PVC is full of controversies and still a matter of discussion; so it is not surprising that it is influencing our understanding of the stabilization area, where a whole range of compounds have been in use since PVC was first used. We have reported on the anomalous behavior of the calcium and zinc stearates when they are preheated,

before their use, to stabilize PVC.<sup>1–4</sup> The latter was found when trying to clarify the role of the CaSt[ZnSt<sub>3</sub>] complex in the stabilization mechanism; such a complex is supposed to be formed during the melting of the metal soaps,<sup>5</sup> during the normal processing of the plastic. Here, the metal soaps behaved in a distinctive way; preheated ZnSt<sub>2</sub> and the mixture of both enhanced the stabilization, while preheated CaSt<sub>2</sub> reduced the induction times to degradation.

Such studies indicated that the same species are formed in the PVC stabilized with and without pretreated metal soaps, being the difference on the time those species appear. This suggested that the very early stages of the stabilization mecha-

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**Table I** Effect of the Costabilizer Rhodiastab-83 on the Preheated Mixtures

Sample PVC Solvic 271GC +	Induction Time, $T_i$ (min)	
	TGA	HCl Evolution
CaSt <sub>2</sub> + ZnSt <sub>2</sub> + R-83	7.5	10.2
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (180°C) + R-83	10.4	11.0
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (150°C) + R-83	12.3	9.9
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (130°C) + R-83	13	9.6
CaSt <sub>2</sub> -ZnSt <sub>2</sub> (100°C) + R-83	7.9	9.9
ZnSt <sub>2</sub> + R-83	3.9	6.4
ZnSt <sub>2</sub> (180°C) + R-83	6.0	5.9
CaSt <sub>2</sub> (180°C) + ZnSt <sub>2</sub> + R-83	3.5	5.9
CaSt <sub>2</sub> (150°C) + ZnSt <sub>2</sub> + R-83	3.9	6.3
CaSt <sub>2</sub> (130°C) + ZnSt <sub>2</sub> + R-83	5.3	8.4
CaSt <sub>2</sub> (100°C) + ZnSt <sub>2</sub> + R-83	6.7	9.2
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (180°C) + R-83 <sup>a</sup>	12.3	10.6 (14)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (150°C) + R-83 <sup>a</sup>	14.1	11.0 (15.4)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (130°C) + R-83 <sup>a</sup>	11.2	11.5 (13.1)
CaSt <sub>2</sub> + ZnSt <sub>2</sub> (100°C) + R-83	7.3	9.3

<sup>a</sup> These samples showed a second  $T_i$  on HCl evolution measurements.

nism are important for the mode of action of the stabilisers.<sup>4</sup>

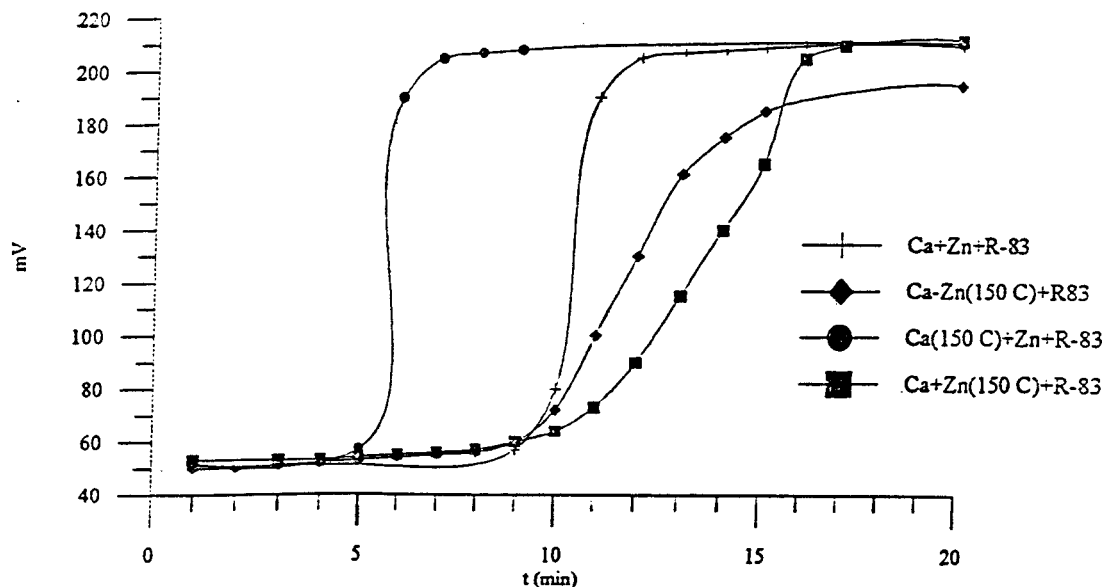
Grossman has showed in a series of articles<sup>6-11</sup> that when stabilizing PVC, it is convenient to use blends of metal carboxylates rather than adding

them separately to the polymer. The reason for this seems to be that the metal soaps associate, not only forming bimolecular species, but also longer chains that can be the actual reacting species in polymeric compositions. He also indicated that when most texts present the mechanism of vinyl stabilization as a stepwise series of reactions, it is more easily rationalized in terms of a concerted mechanism involving mixed metal complexes linked by bidentate carboxylate groups. These results have to much in common with our findings.

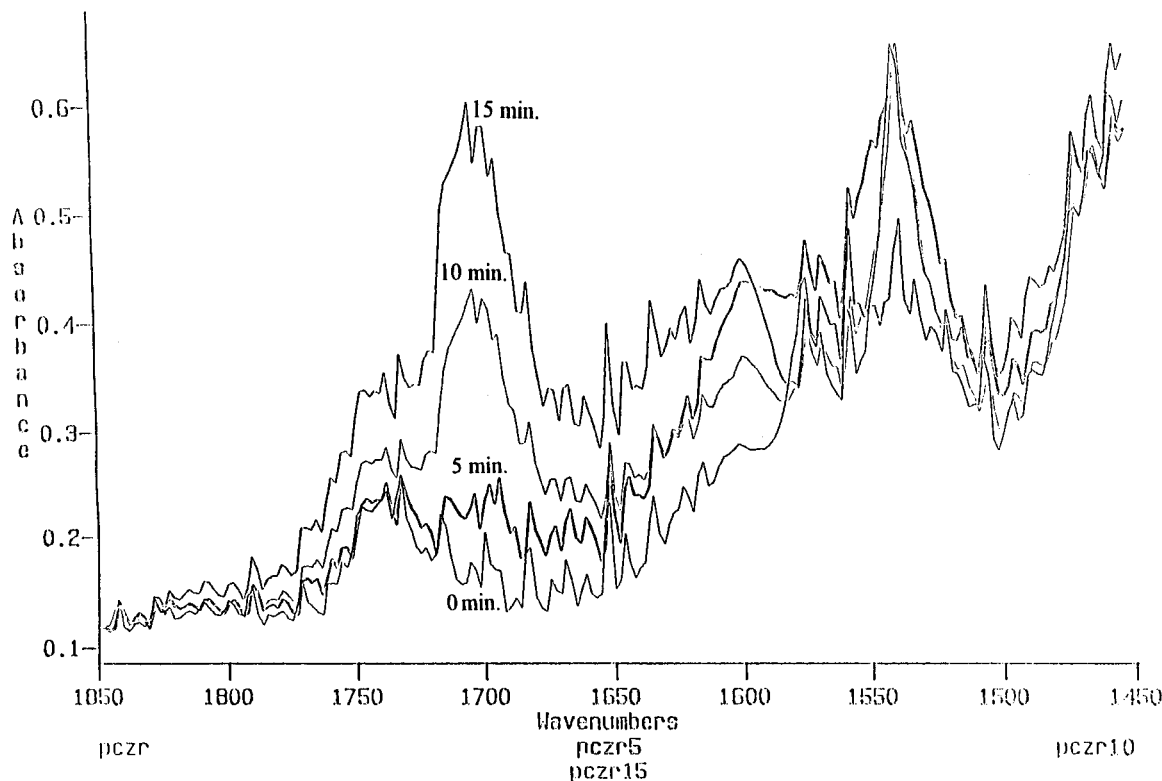
$\beta$ -Diketones are the most popular compounds to provide very good initial color to the PVC; they actually accelerate the degradation time due to their mechanism of action and must be used with a good HCl acceptor. A popular diketone is DBM (dibenzoyl methane), well known for his trade name as Rhodiastab-83.

From model compound studies, Guyot et al.<sup>12-15</sup> have found that they substitute allylic chlorine through a C-alkylation reaction. However, there seems to be a competition from the elimination reaction, which limits the previous one. Despite such competition, GPC-UV traces showed that their grafting on to the polymer is considerable at simulated processing conditions. ZnCl<sub>2</sub> was necessary to catalyze the reaction, because complexation with zinc enhanced their ability to graft into the polymer.

Minsker et al.,<sup>16</sup> on the other hand, found that



**Figure 1** HCl evolution traces for PVC stabilized with preheated metal soaps and Rhodiastab-83 and degraded at 180°C.



**Figure 2** PVC + CaSt + ZnSt + Rhodiastab-83 degraded up to 15 min.

their stabilizing effect was due to their ability to exhibit proton-donating properties and consists of the destruction of primary active sites (carbonallyl groups) for polymer decomposition.

During a comparison of several costabilizers,<sup>17,18</sup> we have shown that a novel short-term costabilizer showed strong complexation with metal stearates. The latter seemed to happen, only in a small degree, for DBM.

It is the intention of this article to show the results obtained when the preheated metal stearates are added along with organic compounds to stabilize PVC. Dibenzoyl methane (Rhodiastab-83), a "short-term" costabilizer is studied in this part, but a "long-term" costabilizer (polyol) will be analyzed in the second part of this series of articles.

## EXPERIMENTAL

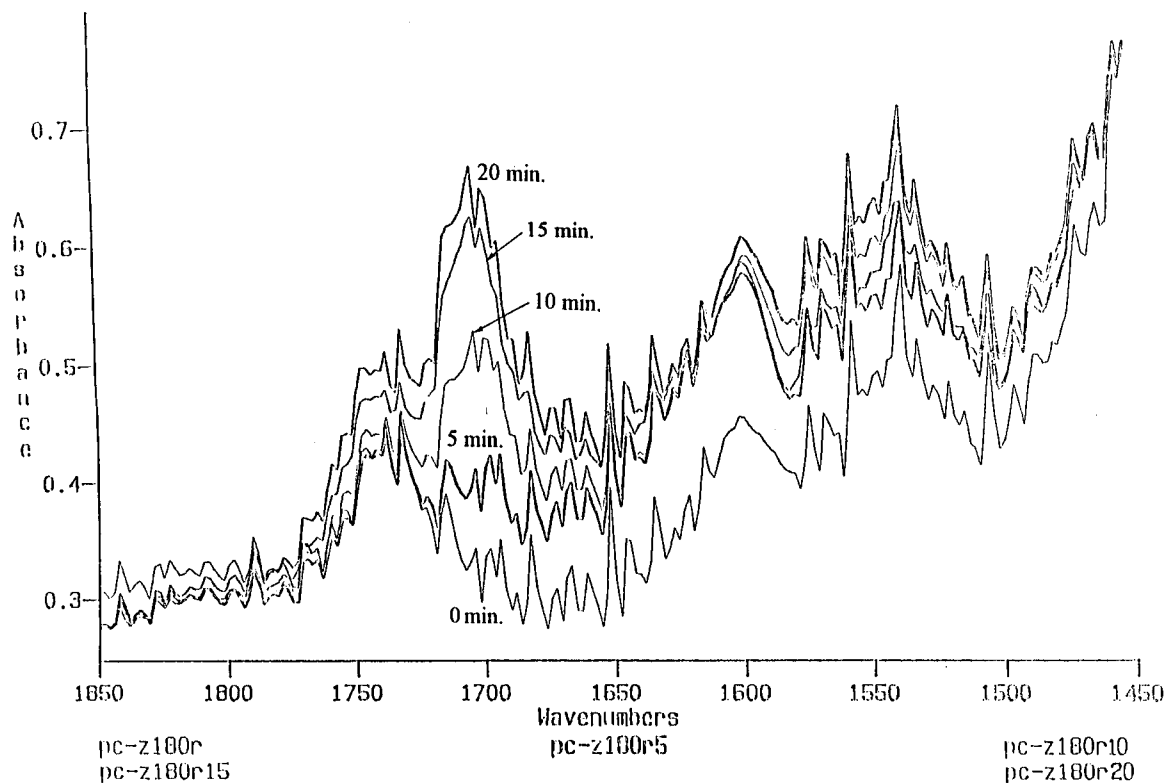
Samples were prepared using industrial PVC Solvic 271GC in powder form doped with 3 phr of the preheated metal stearates and 1 phr of dibenzoyl methane (Rhodiastab 83). All materials were

supplied by Akros Chemicals, Eccles, Manchester, UK.

The preheating treatment of the metal soaps has been reported previously,<sup>1-4</sup> and consists in heating the materials, alone and mixed, in an oven at different temperatures (100–180°C) for 30 min, to finally be ground and added to the resin. The 1 CaSt<sub>2</sub>:2 ZnSt<sub>2</sub> ratio was kept in all the experiments.

The performance of the mixtures was evaluated by means of induction times to degradation using TGA and HCl evolution traces.<sup>1,2</sup> The equipment implemented for the latter consisted of an oil bath controlled at 180°C, where a glass tube containing 500 mg of the sample was introduced as the degradation compartment. A stream of preheated air (60 mL/min), introduced by a pump, swept the evolved HCl into a cell with 100 mL of 0.1M KCl solution, where the potential (mV) was continuously monitored against time.

The same system was used to obtain samples of the mixtures degraded for 5, 10, 15, 20, and 25 min, and such residues analyzed by FTIR (using a BioRad FTS-7 instrument with a reflectance accessory for powder samples); 64 scans were averaged at a resolution of 4 cm<sup>-1</sup>. The spectra were



**Figure 3** PVC + CaSt-ZnSt (180) + Rhodiastab-83 degraded up to 20 min.

baseline corrected and the appearance of carbonyl groups, absorbing at  $1705\text{ cm}^{-1}$ , were followed quantitatively.

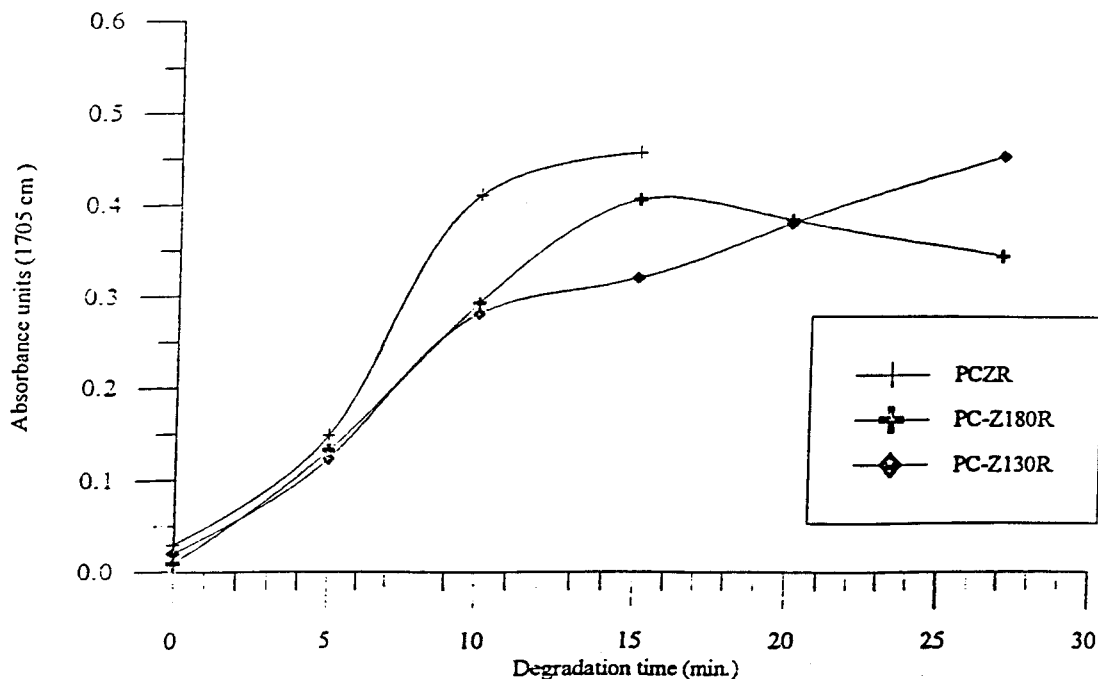
The same powder samples were used for visible reflectance studies. The instrument used was a Perkin-Elmer 559 spectrophotometer, with a mobile head for the evaluation of the solid samples. The head has a photomultiplier with two optic fibres for the output of reference and sample beams from the instrument to the sample. The wavelength range of the head is limited to the visible region (380–800 nm) by the material of the light guides (Pyrex) and measures percentage of reflectance of the powders. The instrument is held at University College of Wales, at Cardiff, UK.

## RESULTS AND DISCUSSIONS

The induction times to degradation ( $T_i$ ) obtained by means of both TGA and HCl evolution are shown in Table I. There are several important features observed when this costabilizer was used along with the preheated soaps. The first and most important is that the  $T_i$ s (induction times)

to degradation are considerably reduced, by both TGA and HCl evolution, and this is a characteristic of the “short-term” costabilizers. These are compounds that substitute allylic chlorines, inhibiting the formation of long polyenes, and hence, no discoloration to the polymer. As a product of those reactions, HCl is produced in larger amounts, accelerating the consumption of the main stabilizers and the formation of the prodegradant  $\text{ZnCl}_2$ , and subsequently blackening the PVC in quite a short time.

Another feature is that the induction times obtained with both techniques do not follow the same trends, as seen when no costabilizer was used.<sup>2</sup> The results from TGA show the trends expected, where the preheating of  $\text{CaSt}_2$  reduces the  $T_i$  and the thermal treatment of the mixture of both metal soaps and of  $\text{ZnSt}_2$  alone delays the fast blackening. On the other hand, HCl evolution only showed this trend when the  $\text{CaSt}_2$  was preheated and when  $\text{ZnSt}_2$  was added alone to the PVC. In the rest of the cases there were no significant changes in the  $T_i$ s through the preheating temperatures. At this point the detailed analysis of the raw data enables us to draw conclusions for such findings.



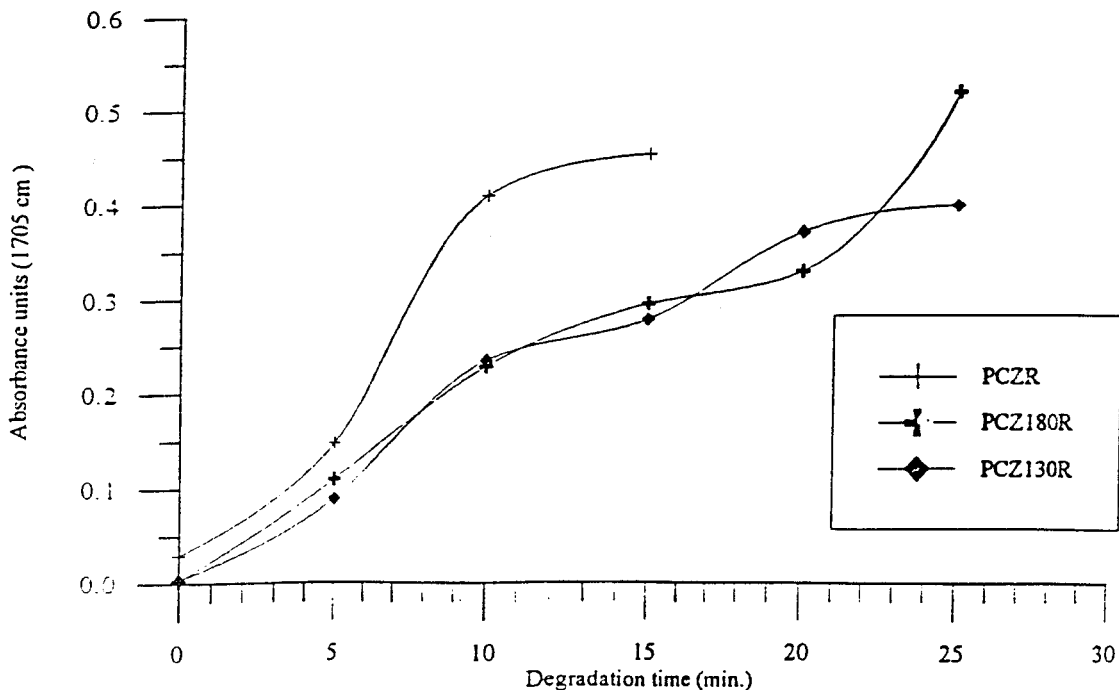
**Figure 4** Carbonyl formation in PVC stabilized with CaSt–ZnSt mixtures (preheated at different temperatures) and Rhodiastab-83 and degraded up to almost total dehydrochlorination.

It has been noticed that the longer the  $T_i$ , the more HCl is evolved during the induction period. This is explained by the fact that the metal soaps are in a different structural conformation induced by the thermal treatment, and that this conformation inhibits the usual behavior (findings of previous reports<sup>1-4</sup>). The preheated ZnSt<sub>2</sub> appears to be reducing the rate of the substitution reaction as well as ZnCl<sub>2</sub> formation, even when the alkylation reaction of the costabilizer in the PVC releases high amounts of HCl. This allows the formation of average size polyene sequences ( $n = 6-8$ ) that give the pale coloration to the polymer without reaching lengths that produce the red and then dark compounds. Figure 1 shows typical traces obtained by HCl evolution with this costabilizer.

The set of samples with the preheated ZnSt<sub>2</sub> shows two possible values of  $T_i$ ; the first one is due to the substitution reactions into the polymer from both the costabilizer and the zinc soap, while the second  $T_i$  comes from the "real" end of the stabilizers and the subsequent fast blackening of the polymer, even though there is not much HCl left to evolve. It is noteworthy to see that the values of the second  $T_i$ s (in parentheses in Table I) show the trend expected and observed by the TGA method.

The preheated mixture of both metal soaps behaves in a quite similar way to the preheated ZnSt<sub>2</sub>; it gave pale colored material from the beginning, with HCl being evolved from the start of the degradation. The increase in the  $T_i$  is not noticed, because instead of giving several rates, it reduced the rate of fast dehydrochlorination, leaving a less dark residue at the end of the total degradation. It agrees with the proposition of a stable complex interacting in the degradation mechanism, which in some way increases the induction time to degradation.

It is noticeable that for these sets of samples the  $T_i$  is always around the value obtained with the control sample (PVC + CaSt<sub>2</sub> + ZnSt<sub>2</sub> + R-83), which indicates that the first stage of the stabilization is controlled by the costabilizer, because it is the only compound that has not been previously treated and is determining the  $T_i$  value; the small differences could be due to minor deviations in curve fitting. This agrees with some authors,<sup>19</sup> whose findings showed that the majority of the metal soaps act merely as HCl acceptors. Hence, the complex CaSt[ZnSt<sub>3</sub>] and the structures produced in the ZnSt<sub>2</sub> with the thermal treatment seem to be reacting less with the hydrochloric acid and reacting more, in a steady state, with the growing polyenes. This effect has not



**Figure 5** Carbonyl formation in PVC stabilized with CaSt + ZnSt (preheated at different temperatures) and Rhodiastab-83 and degraded up to almost total dehydrochlorination.

been seen with the pretreated CaSt<sub>2</sub>, which was simply showing the same trend observed with the samples without the costabilizer, for both TGA and HCl evolution techniques.<sup>2</sup>

The changes in the FTIR bands throughout the degradation time for the samples without the costabilizer has already been published,<sup>2</sup> including the rates of carbonyl formation. Similar studies for the costabilized samples are shown in Figure 2, where changes are not very clear, because the samples degraded so fast that they were only followed until 15 min into the degradation time.

The band seen at 1600 cm<sup>-1</sup>, which mainly corresponds to the costabilizer, is strongly enhanced by the superposition of the complex CaSt[ZnSt<sub>3</sub>] at 5-min degradation. The reduction of this band at 10-min degradation while the carbonylic band increases, suggests that the complex has already reacted, even before the metal soaps, supporting the idea that this new structure is more reactive than the individual soaps during the stabilization mechanism.

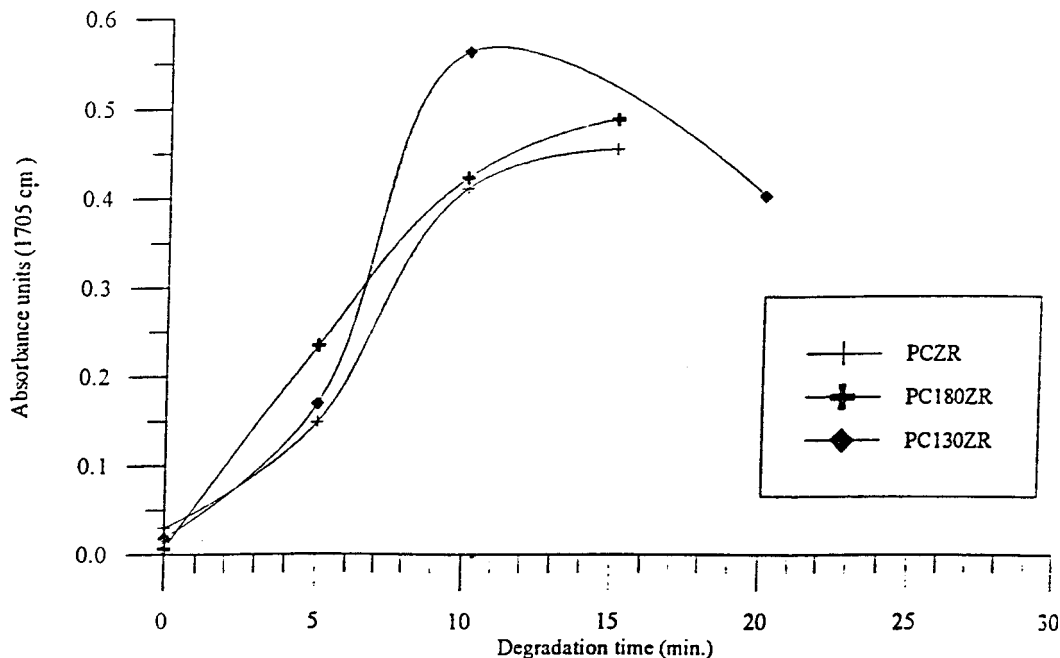
When the complex is added to the mixture from the beginning (Fig. 3), the enhancement of the 1600 cm<sup>-1</sup> band starts since the first 5-min degradation and remains unchanged. The slow disappearance of the metal soaps (1540 cm<sup>-1</sup>) and the

faster appearance of the carbonylic bands are the main features.

The carbonyl formation trends obtained from the FTIR data are shown in Figures 4–6. The control sample was only examined up to 15-min degradation due to the short induction time obtained, and only  $T_p$ s of 130 and 180°C are shown because the others have the same trends, just with intermediate values. It is very noticeable that the rate of formation of these carbonylic groups is considerably high (compared with the uncostabilized samples<sup>2</sup>), especially with preheated CaSt<sub>2</sub> (Fig. 6), which is most likely due to the lack of an induction time during the early stages of the degradation.

The preheating of the mixture of CaSt<sub>2</sub>–ZnSt<sub>2</sub> produced, in general, less carbonyl groups than the control (Fig. 4); showing a slower rate for the preheating temperature of 130°C, and a maximum at 15 min for the  $T_p$  of 180°C. The pretreatment of ZnSt<sub>2</sub> (Fig. 5), on the other hand, produced even less carbonylic groups, without a clear difference between  $T_p$ s of 130 and 180°C. This is consistent with the  $T_i$  results, where the pretreatment of the mixture and the zinc soap always increased the times to degradation.

The preheating of CaSt<sub>2</sub> (Fig. 6) enhanced the



**Figure 6** Carbonyl formation in PVC stabilized with CaSt (preheated at different temperatures) + ZnSt and Rhodiastab-83 and degraded up to almost total dehydrochlorination.

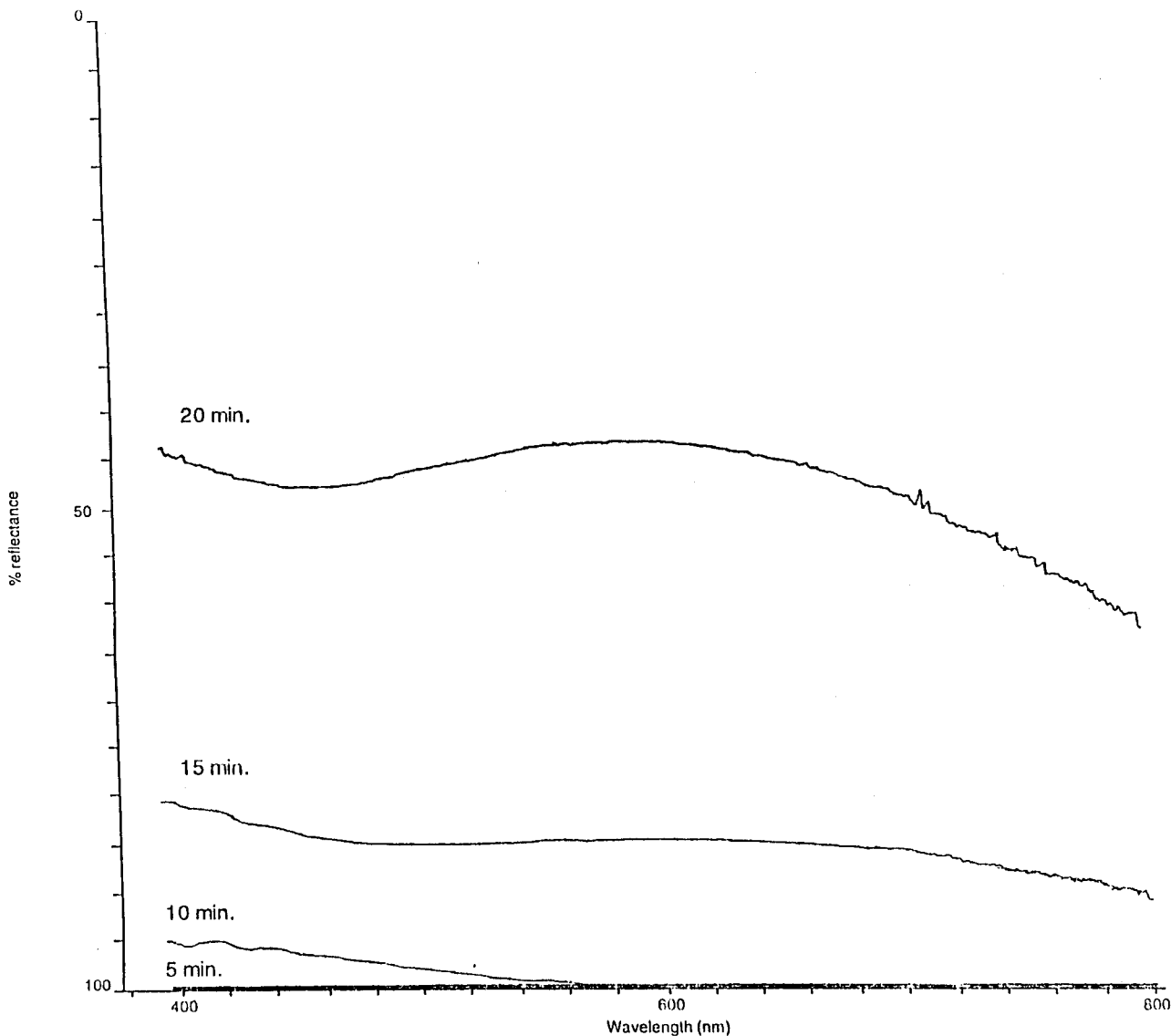
rate of formation and yielded a high amount of carboxylic groups. Such behavior was not surprising, as  $T_i$  evaluations showed the lower values for these samples.

The visible reflectance analyses of the samples were carried out with the aim of correlating the variable colorations obtained throughout the degradation. Figure 7 shows the traces obtained from the control sample without the costabilizer. There are, in general, three regions to observe: the blue region (400 nm), which indicates the length of the double bond sequences (already discussed in ref. 3); the region of the 600 nm, which suggests the presence of colored species and the 800 nm region, which corresponds to the absorption of dark material. For costabilized samples, only reflectance values at such regions will be given.

The reflectance values obtained for the control sample with costabilizer are shown in Table II. The differences, comparing with the uncostabilized control, are in agreement with previous findings, where the blackness of the sample (seen at 800 nm) happens at earlier times. As mentioned before, there was no sample at 20 min because at 15 min it was considerably dark. The data show no other important features, because the shape of the traces are very similar; the only difference being that the small absorptions from

the specific conjugation (400 nm region) at the earlier times of degradation are not present. The lack of this fine detail could be explained by the fact that the costabilizer reacts with the double bonds, forming carboxylic species that shift the wavelength values and avoid the appearance of specific absorptions, as happened for the final degradation time shown in Figure 7.

The use of the preheated mixture  $\text{CaSt}_2\text{-ZnSt}_2$  along with the costabilizer, gave the results shown in Table III. Compared with the no-costabilized sample (shown in ref. 3), there is no formation of specific absorptions, as with the control sample; and there is a high production of absorbing species (lower values of reflectance) from the first 5 min, indicating that the complex is stopping the action of the costabilizer. However, the control by itself (Table II) shows these initial values, demonstrating that the degradation is starting so early that at 5 min there are already absorptions indicating the formation of long polyenes. This also implies that the costabilizer is interacting from the very beginning, and that the rest of the degradation is controlled by the metal soaps which, due to the pretreatment, are not allowing a total blackness of the sample after 20 min of degradation. The same effects have been observed by HCl evolution and FTIR analyses.



**Figure 7** Visible reflectance of PVC + CaSt + ZnSt degraded up to 20 min.

The differences observed for these samples between the preheating temperatures ( $T_p$ ) of 180 and 130°C show exactly the same trends as for the uncostabilized ones (ref. 3). Actually, because this was expected, there were no evaluations for the  $T_p$ s of 100 and 150°C. The first 10 min of degradation give the same values and for 15 and 20 min, and there is an increment on the values for the  $T_p$  of 180°C. This is in agreement with previous findings where the temperatures of 130 and 180°C might be sufficient to destroy part of the complex formed, and so reducing its beneficial effects.

Table IV shows the percentage of reflectance values obtained when ZnSt<sub>2</sub> alone was preheated

at 180 and 130°C, mixed with CaSt<sub>2</sub> and Rhodistab-83, and used to stabilize PVC. Again, a lack of specific absorptions due to the formation of carbonylic species was noted. The difference with the no-costabilized sample is rather small, considering the normal effect of the costabilizer addition to the metal soaps (as in control samples, Fig. 7 and Table II), where the reflectance values were considerably altered. This means that, in general, the metal soaps control the stabilization patterns of the polymer. Because there is less ZnSt<sub>2</sub> available in the media (due to the preheating), there is less formation of ZnCl<sub>2</sub> to catalyze the C-alkylation reaction of the costabilizer in the polymer. However, there seems to be some of this this reac-



**Table II Reflectance Values for the Control PVC + CaSt<sub>2</sub> + ZnSt<sub>2</sub> + R-83**

Degradation Time (min)	Percentage of Reflectance at:		
	400 nm	600 nm	800 nm
0	100	100	100
5	91	96	98
10	61	79	88
15	15	26	42
20	—	—	—

tion happening, because there is a lack of specific absorptions on the traces.

The preheating of CaSt<sub>2</sub>, which was mixed with ZnSt<sub>2</sub> and the costabilizer to stabilize PVC, gave the results shown in Table V. The data very clearly show the fast blackening of the samples: at 15 and 20 min no data were taken because the samples were completely black. It is obvious that the shortening of the induction times are due to the combined effects of both the preheated calcium soap and this short-term costabilizer, because without the costabilizer (ref. 3) the data indicates a slower process of blackening. This indicates that there is no significant need for the calcium soap in the costabilization mechanism; but it does prove that it is needed for the synergism with the zinc stearate.

The differences in reflectance values between the  $T_p$ s of 180 and 130°C indicate that the latter temperature is enough to produce changes in the calcium soap, even without melting it. This is consistent with data on carbonyl formation from FTIR and with HCl evolution results, which showed some differences in their values with respect to the control sample.

**Table III Reflectance Values for PVC + CaSt<sub>2</sub> - ZnSt<sub>2</sub>( $T_p$ ) + R-83**

Degradation Time (min)	Percentage of Reflectance at:					
	$T_p = 180^\circ\text{C}$			$T_p = 130^\circ\text{C}$		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	98	100	100	98	100	100
5	93	98	99	94	99	100
10	72	92	95	77	93	96
15	42	67	77	51	77	85
20	25	51	63	35	61	73

**Table IV Reflectance Values for PVC + CaSt<sub>2</sub> + ZnSt<sub>2</sub>( $T_p$ ) + R-83**

Degradation Time (min)	Percentage of Reflectance at:					
	$T_p = 180^\circ\text{C}$			$T_p = 130^\circ\text{C}$		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	100	100	100	100	100	100
5	91	97	98	92	97	99
10	76	90	95	75	90	93
15	62	82	89	62	84	89
20	50	74	82	44	68	76

## CONCLUSIONS

The addition of the  $\beta$ -diketone Rhodiastab-83 (Dibenzoyl methane) as a costabilizer to the main stabilizer system of CaSt<sub>2</sub> and ZnSt<sub>2</sub> for PVC, reduces the induction time to degradation to improve the initial color. This is the reason for it being known as a "short-term" costabilizer. The latter has been verified by all the experimental techniques used in this article.

The preheated mixture of metal soaps, along with the costabilizer, delayed the fast blackening of the polymer, but mainly showed a reduction in the rate of dehydrochlorination, which subsequently produced a less black material. Preheated ZnSt<sub>2</sub>, along with Rhodiastab-83, delayed the induction times to degradation as well, and showed a second rate of dehydrochlorination quite clearly in the HCl evolution traces, indicating the separated consumption of the compounds during the stabilization mechanism. The results from preheated CaSt<sub>2</sub> were not very clear, because it con-

**Table V Reflectance Values for PVC + CaSt<sub>2</sub>( $T_p$ ) + ZnSt<sub>2</sub> + R-83**

Degradation Time (min)	Percentage of Reflectance at:					
	$T_p = 180^\circ\text{C}$			$T_p = 130^\circ\text{C}$		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	100	100	100	100	100	100
5	81	90	95	91	98	100
10	9	10	27	27	36	55
15	—	—	—	—	—	—
20	—	—	—	—	—	—

siderably reduced the induction times to degradation, leaving a few samples available for running the experiments. All  $T_i$ s results were in some way corroborated with carbonyl formation and visible reflectance studies.

As a general conclusion, it can be mentioned that the effect of the costabilizer in the PVC stabilization mechanism appears not to be significantly altered by the addition of thermally pretreated metal soaps. It has been seen that both effects behave mostly by separate mechanisms, and that the apparent new structures formed during the preheating of the metal stearates do not interfere with the normal costabilization mechanism.

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