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THE EFFECT OF THERMAL PROCESSING ON PVC—II
THE EFFECT OF LUBRICANTS AND STABILIZERS

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Abstract—The effects of lubricants and a tin maleate stabilizer on the mechanochemical and thermal degradation of PVC during processing have been studied at 170° and 210°. The protective mechanism of the two types of additive were found to be complementary in that the lubricants reduced the severity of the mechano-chemical process whereas the tin maleate stabilizer reduced the rate of hydrogen chloride elimination during the second stage by reacting with allylic chlorine, with conjugated unsaturation and with hydrogen chloride.

INTRODUCTION

It has been shown [1, 2] that the effect of thermal processing on unstabilized PVC was to introduce into the polymer unsaturation and peroxides as a consequence of mechano-chemical shearing of the polymer chains during the first minute in an efficient mixer. This mechano-chemical process in the presence of oxygen is associated with peroxy-gel formation and is primarily responsible for the initiation of the subsequent thermal and thermal oxidative processes.

The purpose of the present study is to examine the effect on the physical and chemical processes involved of three conventional additives for PVC (Wax E, an ester lubricant, calcium stearate (Ca St), a stabilizer/lubricant and a commercial stabilizer consisting primarily of dibutyltinmaleate (SnM) and a three-component synergistic mixture of these additives.

EXPERIMENTAL

Materials

PVC was a commercial suspension polymer (Solvic 223) ex Solvay and Cie. The tin stabilizer (SnM) was a commercial product (Irgastab T_{290}) ex Ciba-Geigy Limited, of which dibutyltinmaleate was the main component. Infrared spectroscopic analysis suggested that this additive contained a minor amount ($\simeq 5\%$) of a hindered phenolic antioxidant. Calcium stearate (Ca St) was Analar grade ex BDH Chemicals. The lubricant was a commercial product, Wax E, ex Hoechst AC.

Procedure

PVC processing was carried out in a proto-type RAPRA torque rheometer as described previously [2]. The measurement of the formation of solvent insoluble gel and of other chemical changes occurring in the polymer have also been previously described [2].

RESULTS

In the previous study of unstabilized PVC [2] it was found that several parameters could be used to elucidate the chemical and physical processes occurring during the processing of PVC. These were (i) the torque generated at constant shear in the mixer; (ii) the gel content of the polymer; (iii) ethylenic unsaturation developed in the polymer as measured (a) chemically, (b) u.v. absorption at 230 nm and (c) by i.r. absorption at 2850–5 cm^{-1}; (iv) peroxide by chemical measurement; (v) total colour increase by colourimeter and (vi) conjugated unsaturation by u.v. absorbance at 275, 310 and 365 nm which correlated closely with (v).

The above parameters show three related but different kinds of behaviour with time.

(a) An initial sharp maximum, followed by a decrease to give an induction period before a second increase. This behaviour is examplified in Fig. 1 which shows development of torque and the formation of gel in PVC stabilized with a tin maleate stabilizer (2.5 g/100 g).

(b) An initial rapid increase to a maximum followed by an induction period before a further increase. Figure 2 shows such typical behaviour for unsaturation (2.5 g/100 g SnM). It also applies to the u.v. absorbance at 230 nm and to colour development.

(c) An initial induction period followed by rapid growth. This is exemplified for peroxide in stabilized PVC (Fig. 2).

Two main purposes of this examination were to determine as far as possible (a) the sequence of physical and chemical events from the values of t_1 (min) for each parameter during the mechano-chemical stage of the reaction and of t_2, the induction period (in min) to the extensive thermal oxidative degradation which is a measure of the lifetime of the polymer under these conditions and (b) the effect of lubricants and stabilizers on the extent of these changes (A, the maximum value achieved and R, the rate of the change at the end of the induction period). It is clear from Table 1 that the initiating event is the generation of a high torque, followed closely by the development of solvent insoluble gel and unsaturation in the polymer. Only in the case of PVC, without additives, was there rapid concomitant formation of peroxides [1, 2]. In the PVC containing the two lubricants, the initial mechano-chemically formed peroxide was missing [see Fig. 3, (a) and (b)] and its formation was auto-catalytic from the beginning. Visible colour is

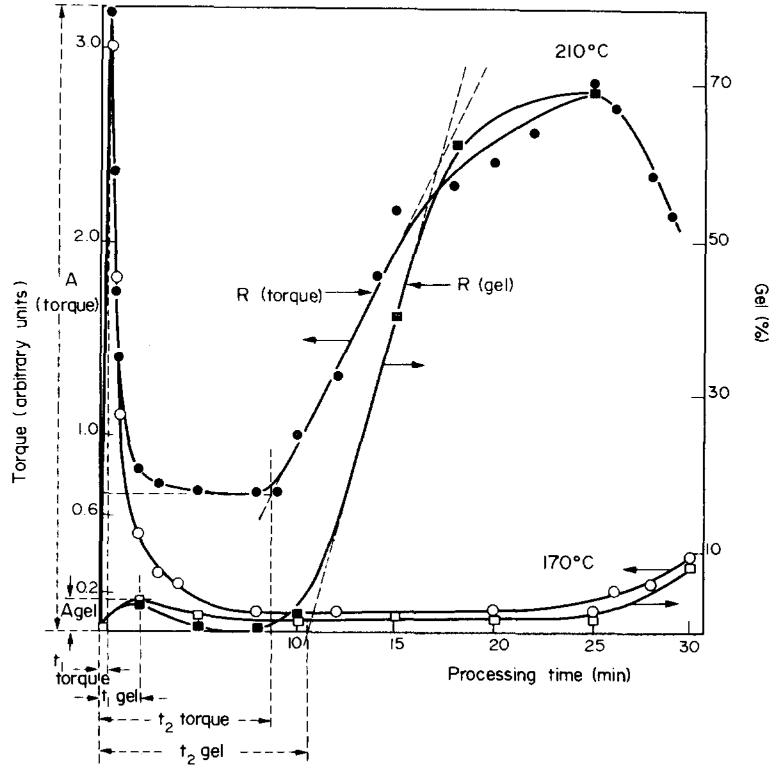


Fig. 1. Effect of processing time on applied torque and on gel formation in PVC stabilized with a tin maleate (SnM) stabilizer (2.5 g/100 g) (processing temperatures indicated on the curves). A = value of initial maximum, t_1 = time to initial maximum, t_2 = induction period to further increase, R = rate of increase at the end of the induction period.

also formed linearly from zero time in these three systems. In the presence of the tin maleate stabilizer, no further increase in unsaturation or of peroxides could be observed until the end of the induction period t_2. The three component synergistic system behaved similarly [see Fig. 3, (c) and (d)].

It is instructive to compare the effects of the lubricants with the tin stabilizer on the extent of the mechano-chemical processes (Table 1). Both Wax E and calcium stearate reduced to less than one half the torque (A) experienced by the polymer. The tin maleate stabilizer on the other hand actually increased it and significantly increased the ethylenic unsaturation relative to the control whereas the Wax E lubricant had the opposite effect. The effect of calcium stearate on mechano-chemically formed unsaturation was less unequivocal. However the lubricants affected the thermal colour formation in opposite directions (see Table 1). Wax E retarded it; calcium stearate accelerated it. Although the primary stage

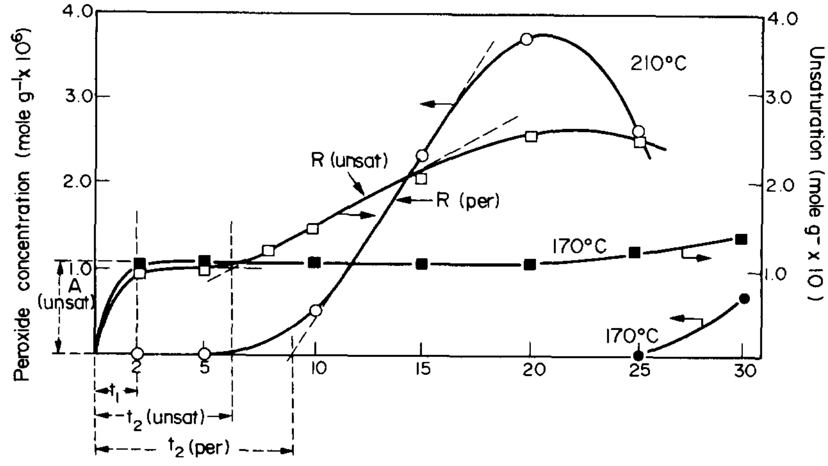


Fig. 2. Effect of processing time on the formation of unsaturation and of peroxides in PVC stabilized with a tin maleate (SnM) stabiliser (2.5 g/100 g) (processing temperatures indicated on the curves).

Table 1. Processing parameters for PVC processed at 210°

				Unsaturation			
		Torque	Gel	(a) Chemical changes	(b) u.v. 230 nm	Peroxide	Total colour change
Control (no additive)	t_1	0.25	0.75	1.0‡	1.0	2.0	*
	A	3.0	6.0	0.6	0.15	0.8	*
	t_2	5.0	5.0	‡	5.0	8.0	*
	R	0.26	7.20	$\simeq$0.73	0.09	0.085	5.8
Wax E	t_1	0.25	0.0	$\simeq$1.0‡	$\simeq$1.0‡	†	*
	A	1.35	*	0.4	0.12	†	*
	t_2	6.0	*	‡	‡	†	‡
	R	0.3	6.0	$\simeq$0.77	0.08	0.09	5.0
Calcium stearate	t_1	0.25	2.0‡	$\simeq$1.0	1.0	†	*
	A	1.3	4.5	0.9	0.15	†	*
	t_2	3.5	4.0	‡	‡	†	‡
	R	0.24	11.0	0.47	0.24	0.33	6.0
Tin maleate	t_1	0.3	2.5	2.0	1.5	§	2.0
	A	3.3	3.0	0.9	0.25	§	5.0
	t_2	8.0	11.0	7.0	11.0	9.0	8.0
	R	0.2	8.2	0.15	0.16	0.4	0.73
Synergistic mixture	t_1	0.25	2.0	2.0	1.0	§	2.0
	A	1.4	5.0	0.9	0.27	§	8.0
	t_2	8.0	9.5	10.0	13.5	8.0	10.0
	R	0.3	6.0	0.11	0.12	0.35	0.29

* No induction period, linear rate; † No induction period, auto-accelerating; ‡ No induction period, inflexion; § Not detected during induction period.

colour formation was at least as rapid in the tin maleate stabilized polymer as in the control, colour formation rapidly auto-retarded in the same way as chemically measured unsaturation to give an induction period (see Fig. 4) before further increase due to thermal processes. Initial colour production was 60% higher in the synergistic mixture but the induction period was also 25% longer. Another significant difference between the lubricants and the thermal stabilizer was that the latter markedly reduced the rate of colour formation at the end of the second stage. Wax E had a small effect on the rate of colour formation at 210° but markedly decreased it from the beginning of processing at 170° (see Fig. 5). However, none of the additives was able to eliminate or even substantially reduce the formation of unsaturation and colour (*A*) during the first minute of processing. Reducing the temperature from 210° to 170° had little effect on the extent of formation of unsaturation. *A* (torque) was always higher and *A* (gel) was generally lower, but all the measures of initial unsaturation were not greatly different. The most significant finding was that the length of the secondary induction period (t_2) for each of the properties measured was approximately the same, at a given temperature but varied with the stabilizer system used. Thus for the control at 210°, t_2 was about 5 min (t_2) peroxide was slightly longer); at 170° it was about 15 min. For the tin maleate (SnM) system the values of t_2 were approx 10 min at 210° and 25 min at 170°. There was some evidence however that an increase in unsaturation always slightly preceded the other changes during this second stage. This can be seen in Figs 2 and 3. A study of the formation of conjugation in PVC containing the synergistic stabilizer shows (see Fig. 6) that the u.v. absorptions at 280 and 325 nm begin to grow even after 15 min at 170° indicating that this must be the primary change in the second stage of thermal oxidative degradation from which all others follow.

Figure 7 shows the decay of the carboxylate i.r. absorbance at 1575–85 cm^{-1} due to tin maleate at both 210 and 170°. Both the total sample and the solvent soluble portion of the polymer give curves of similar slope. The complete disappearance of the carboxylate absorption 210° is in reasonable agreement with the length of the induction period (t_2 = 10 min) to colour formation at the same temperature. At the lower temperature over 50% of the original stabilizer still remained at the end of the colour induction period but the post-induction period rate was very much lower than that of the unstabilized control; during this lower rate period, the stabilizer concentration reduced much more rapidly.

The decrease in the carboxylate concentration was paralleled by an increase in ester. This was initially unsaturated [2] ($\simeq$ 1725 cm^{-1}) shifting to saturated, (1745 cm^{-1}). At 210° this rose to a maximum during the induction period and began to decrease slowly at the end of the induction period (see Fig. 8, which relates to PVC stabilized with the tin maleate stabilizer. The synergistic system showed an identical behaviour). At 170° the end of the induction period was marked by a sharp increase in the rate of ester formation which levelled at about 30 min. A study of the formation of carbonyl at 1778 cm^{-1} and the associated peak at 1848 cm^{-1} due to maleic anhydride showed similar behaviour (Fig. 9). Again at 210° there was a steady increase in concentration up to the end of the induction period, followed by a slower fall. A sample of film made from PVC processed at 210°

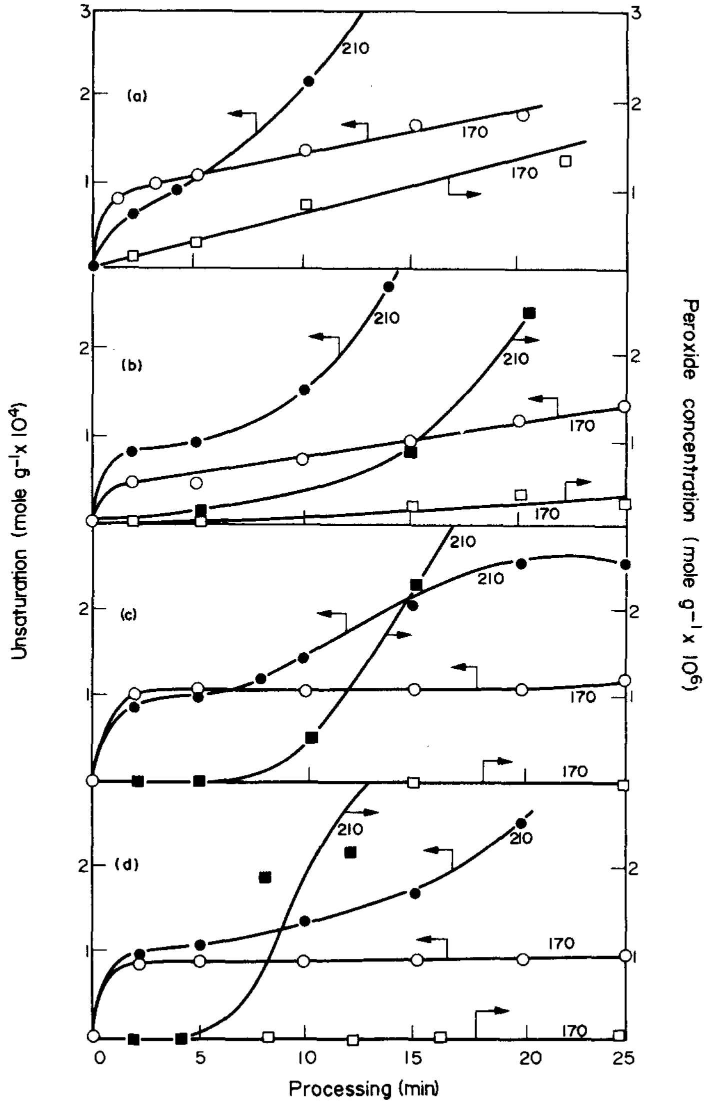


Fig. 3. A comparison of the growth of unsaturation and of peroxides in PVC containing (a) Wax E (0.65 g/100 g); (b) calcium stearate (Ca St) (0.8 g/100 g); (c) tin maleate (SnM) (2.5 g/100 g) and (d) a synergistic mixture of the three additives (processing temperatures indicated on the curves).

almost to the end of the induction period was treated with boiling water for 45 and 105 min and the change in the i.r. spectra was observed (Fig. 10). The original anhydride absorption was substantially replaced by the carbonyl absorption of the free acid (1715–20 cm^{-1}) and the corresponding carboxylate absorptions at 1630 and 1603 cm^{-1}). At 170° there was a slower increase in concentration up to the end of the induction period followed by a sharp increase in the rate of formation up to 25 min. This is in turn followed by a slower fall in concentration. It is clear from this that maleic anhydride itself is involved in the post induction period (t_2) retardation process. In parallel with the formation of maleic anhydride, an i.r. absorption at 342 cm^{-1} grew at both 210° and 170° (see Fig. 11). The intensity of this absorption was similar after 8 min at 210° to that at 170° after 25 min.

The early formation of gel in PVC containing the tin maleate stabilizer (see Fig. 1) is somewhat unexpected. It is non-peroxidic since peroxide could not be detected in the polymer until the end of the induction period (Fig. 2). The gel did however contain both carbonyl (1730 cm^{-1}) and hydroxyl (3450 cm^{-1}) and their concentration changed with time in an entirely parallel manner. This is shown for carbonyl in Fig. 12 but the maxima for hydroxyl occurred at exactly the same time for the two temperatures.

PVC containing calcium stearate also showed the initial presence of carboxylate by i.r. (1535, 1570 cm^{-1}) which decayed rapidly (2–5 min at 210° and 5–10 min at 170°). As in the case of tin maleate, ester (1740 cm^{-1}) is formed concomitantly, within 2 min at 210° and within 10 min at 170° (Fig. 13). Free carboxylic acid (1705 cm^{-1}) and hydroxyl (3420–70 cm^{-1}) were formed at the same time (maximum at 4 min at 210° and 10 min at 170°).

Molecular weight changes

Figure 14 shows the effect of increasing processing time at 210° on the molecular weight distribution of the solvent-soluble phase of PVC containing calcium

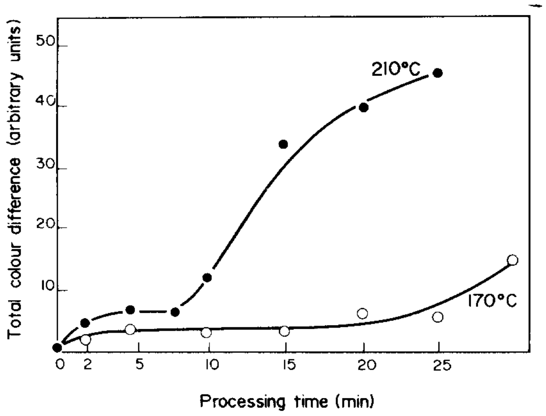


Fig. 4. Colour change during processing of PVC containing SnM (2.5 g/100 g) processing temperatures indicated on the curves).

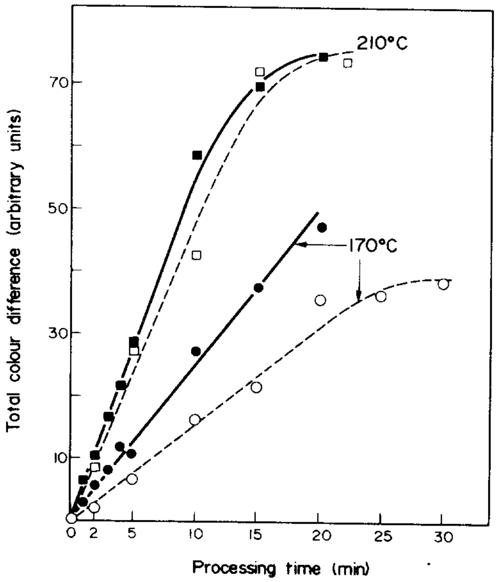


Fig. 5. Effect of lubricant (Wax E, 0.65 g/100 g) on the colour formation in unstabilized PVC (processing temperatures indicated on the curves). Full curves without Wax E, hatched curves with Wax E.

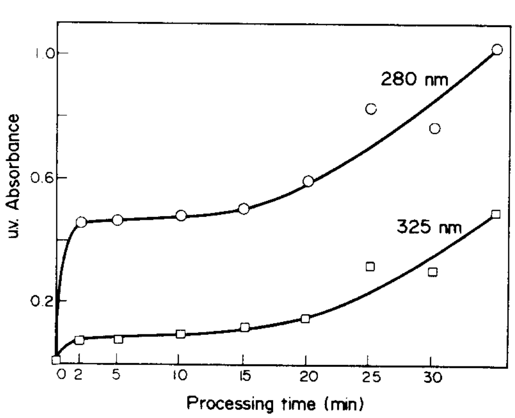


Fig. 6. Growth of u.v. absorbances at 280 and 325 nm with processing time at 170°C in PVC stabilized with SnM (2.5 g/100 g).

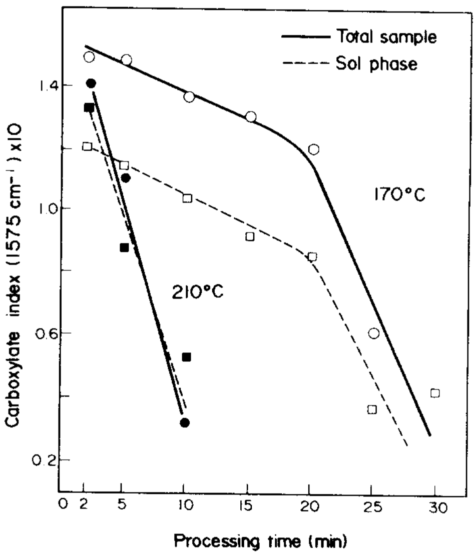


Fig. 7. Decay of the tin maleate carboxylate i.r. absorbance (1575 cm^{-1}) in PVC containing a synergistic mixture of tin maleate (2.5 g/100 g) and Wax E (0.65 g/100 g). —— Total sample, ----- soluble phase (processing temperatures indicated on the curves).

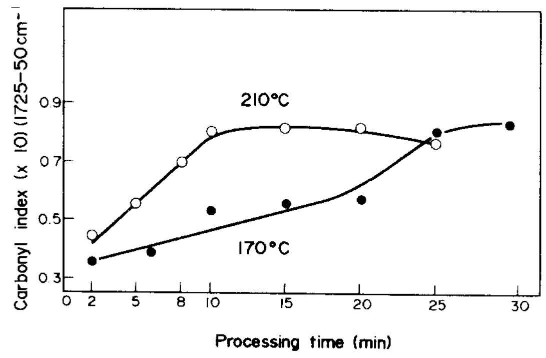


Fig. 8. Growth of the i.r. absorbance (1725–50 cm^{-1}) due to ester in PVC stabilized with SnM (2.5 g/100 g) during processing (processing temperatures indicated on the curves).

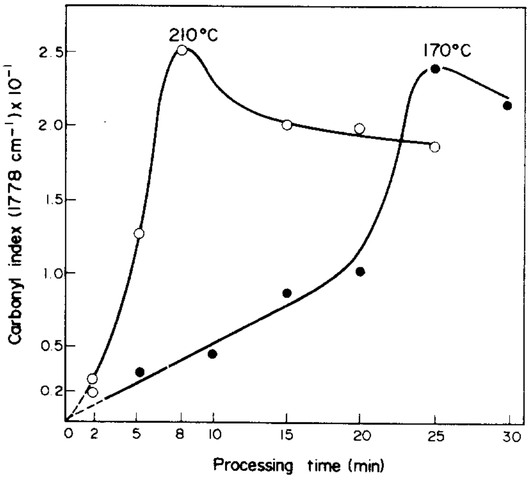


Fig. 9. Growth of the i.r. absorbance (1178 cm^{-1}) due to maleic anhydride in PVC stabilized with SnM (2.5 g/100 g) during processing (processing temperatures indicated on the curves).

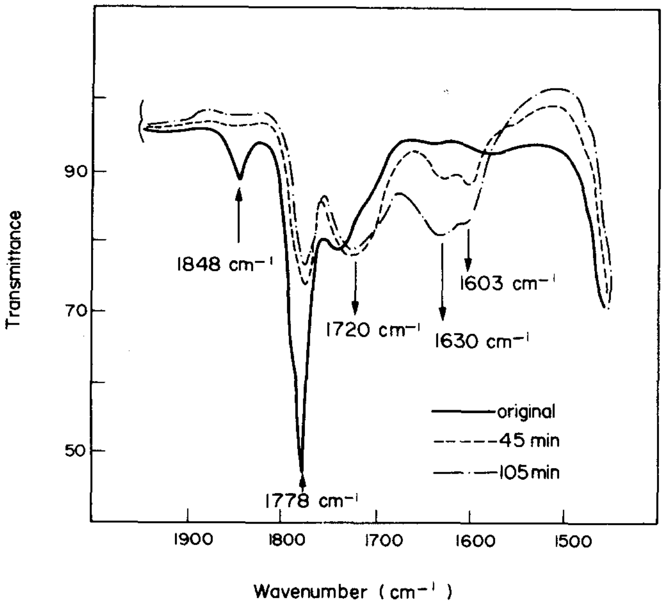


Fig. 10. i.r. Absorbance at 1178 cm^{-1} of PVC containing SnM (2.5 g/100 g) after processing for 8 min at 210°, before and after treatment with distilled water at 100°. —— Original film, ----- 45 min treatment, -·-·-·- 105 min treatment.

stearate. This behaviour, an initial increase followed by a decrease in molecular weight with some broadening, is typical of all the systems studied, the main difference being the time at which the molecular weight maximum begins to decrease. The plot of log M against time (Fig. 15) gives an indication of this. It can be seen (Fig. 15) that only in the case of Wax E [curve (b)] is there no appreciable increase in molecular weight. The subsequent decrease is similar to the control. In the case of the tin stabilizer and the synergistic system, the initial increase in molecular weight was not affected by the stabilizer but the rate of the subsequent fall was considerably reduced.

DISCUSSION

As a result of the study of the changes in PVC during thermal processing in the absence of additives [1, 2] it was shown that two distinct stages of degradation occurred. The first stage was associated with the conditions of high shear during the melting process which led to mechano-chemical scission of polymer chains and the formation of unsaturation and peroxide-containing gel. The second stage, which followed an induction period, resulted in a further increase in unsaturation associated with the formation of a more stable gel and an increase in torque. The results presented in the present paper show that the same sequence occurs in the presence of additives. It is particularly clear from Figs 2 and 6 that the primary change in the second stage of degradation is an increase in unsaturation, with associated colour, which leads to an increase in gel content and torque.

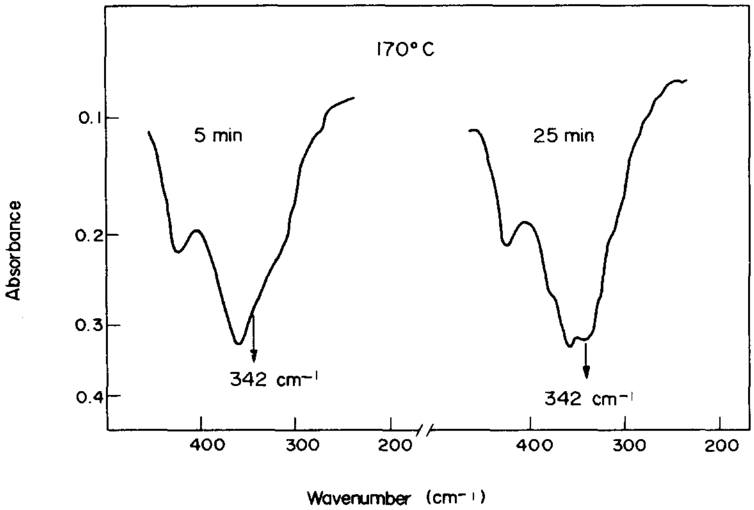


Fig. 11. i.r. Absorbance at 342 cm^{-1} of PVC containing SnM (2.5 g/100 g) processed for 5 min and 25 min at 170°.

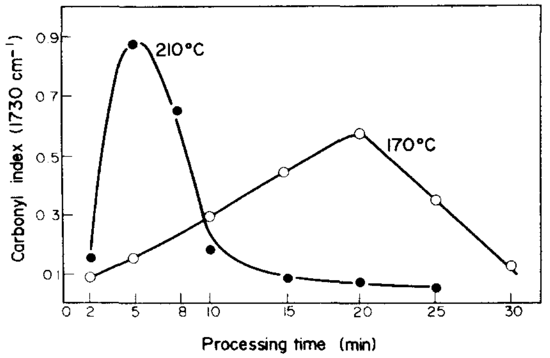


Fig. 12. Change in carbonyl index (1730 cm^{-1}) of PVC containing SnM (2.5 g/100 g) with processing time (processing temperatures indicated on the curves).

Peroxide formation is also a secondary consequence of the increase in unsaturation.

It is clear from Table 1, which tabulates the rate and extent of the change in the chosen parameters, that the three processing additives affect the two stages of thermal degradation differently. Both lubricants reduced the inital torque (*A* torque) and the initial gel formation (*A* gel) relative to the control with no additives (see Table 1). Wax E also decreased the initial unsaturation (*A* unsat) but calcium stearate appeared to have little effect on this parameter. The tin maleate stabilizer actually increased torque and unsaturation during the initial stage but gel formation was reduced. The initial peroxide maximum observed in the case of the control was not found for any of the additives. In the case of Wax E and calcium stearate, no induction periods to the formation of peroxides were observed and, particularly in the case of calcium stearate, the formation of second stage products was accelerated [see Fig. 3, (b)]. The tin maleate stabilizer on the other hand gave a clear induction period to peroxide formation and to the formation of second stage unsaturation which precedes it.

It seems clear then that the lubricants exert a favourable effect during the first stage by reducing the mechano-chemical processes which lead to the formation of unsaturation species which are involved in the subsequent thermal activation of the polymer. They do not appear to play a positive role in the second stage. The tin stabilizer on the other hand appears actually to increase the rate and extent of the initial formation of unsaturation but it also effectively stabilized the initially formed unsaturation and inhibited the formation of peroxides.

These characteristics were paralleled in the changes in molecular weight which occurred in the soluble phase of the polymer. Figure 15 shows that only the Wax E lubricant significantly decreased the initial cross-linking process which leads to increased molecular weight and this was associated with decreased formation of unsaturation and insoluble gel. The tin stabilizer had no effect on the initial formation of cross-links and there was again a suggestion that these may have increased. The subsequent molecular weight reduction which was marked in the case of the PVC control and those containing lubricants was appreciably retarded with tin maleate, consistent with the initial absence of peroxides (see Fig. 3).

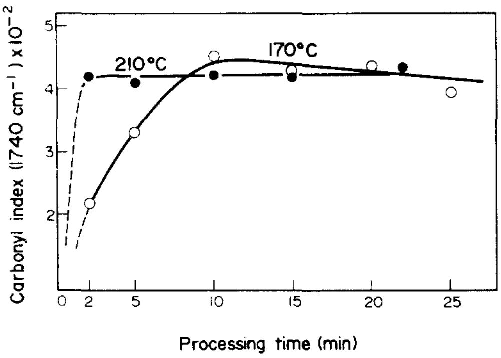


Fig. 13. Change in carbonyl index (1740 cm^{-1}) of PVC containing Ca St (0.8 g/100 g) with processing time (processing temperatures indicated on the curves).

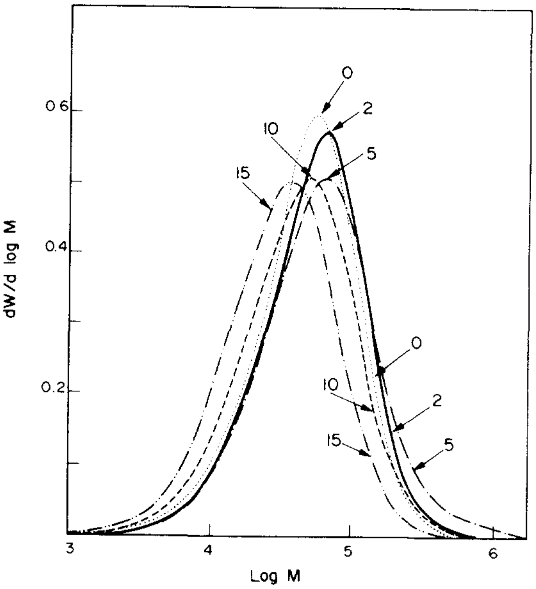


Fig. 14. Molecular weight distribution of PVC containing Ca St at various processing times at 210° (numbers on curves are processing times in mins).

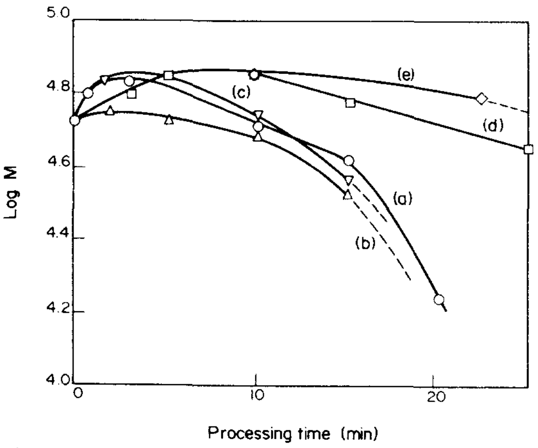
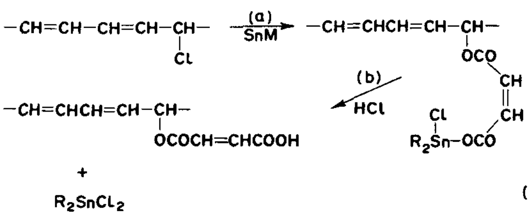


Fig. 15. Variation of maximum log M with processing time of PVC containing additives at 210°, (a) control (no additive; (b) Wax E (0.6 g/100 g); (c) Ca St (0.8 g/100 g); (d) SnM (2.5 g/100 g) and (e) synergistic combination.

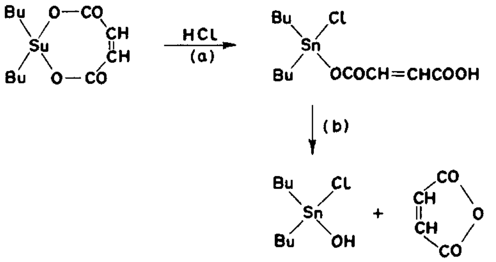
The chemical processes involved in the action of the tin maleate stabilizer are clearly demonstrated by the disappearence of the carboxylate group (Fig. 7) during the induction period (t_2) and the concomitant formation of ester (Fig. 8). This accords with the view [3] that a primary function of the tin maleate stabilizer is to displace allylic chlorine associated with unsaturation present in the polymer.



(1)

It is significant in this connection that an additional function of the maleate is to react with conjugated unsaturation produced during the induction period. There is no significant reduction in the initial unsaturation but the shift in the ester carbonyl absorption from 1725 cm^{-1} initially to 1745 cm^{-1} towards the end of the induction period indicates that the maleate group undergoes a Diels–Alder reaction with conjugated unsaturation formed [4]. Both this reaction and reaction (1) involve cross-linking processes, reflected in the formation of gel during the induction period (see Fig. 1) i.r. Examination of this gel showed the expected presence of carbonyl which rose to a sharp maximum and then decreased (Fig. 12). More surprising is an entirely parallel increase in hydroxyl which can only be accounted for readily on the basis of the reaction of the ester formed in reaction (1), or its Diels–Alder adduct, with HCl to give a mono-ester of maleic acid [1(b)].

It is clear from the formation of maleic anhydride (Fig. 9) that direct attack of HCl at the tin-ester bond occurs during the induction period.



(2)

This mechanism, previously proposed on the basis of radio-chemical evidence [4], is consistent with the observation that an i.r. absorption peak at 342 cm^{-1} due to the Sn–Cl bond grew during the induction period (Fig. 11) and reached a similar absorbance at the end of the induction period at the two processing temperatures. The ready hydrolysis of the maleic anhydride in the presence of boiling water to give free acid (Fig. 10) is also strong supporting evidence for the above reaction which may also account for the subsequent slow consumption of the anhydride after the end of the induction period (Fig. 9).

A significant feature of stabilizing systems containing tin maleate (both alone and as a synergist) is that at 170°, over 50% of the tin stabilizer is still present in the polymer at the end of the colour induction period (t_2 col). At this point, the rate of decrease in concentration increases (Fig. 7) and this is paralleled by an increased rate of maleic anhydride formation. These results indicate a change in mechanism from reaction with allylic chlorine to reaction with HCl; the reason is not clear since it does not occur at 210° but it must correspond to a sharp rise in the HCl concentration in the system.

Although a parallel series of reactions occurred with calcium stearate involving esterification of allylic chlorine [5, 6] and direct attack of HCl on the salt, these processes are much less effective than the tin maleate in retarding the degradation processes occurring in PVC. This is particularly noticeable in the absence of an induction period (t_2) to unsaturation or colour formation. The presence of an inflexion indicated a slight retardation only. It seems likely that the lubricating effect of calcium stearate which leads to the reduction in applied torque is primarily associated with the formation of the free acid which is known to have lubricating properties [7].

Since the individual additives affect the two stages of PVC degradation in different ways, it is now understandable that they will show a co-operative effect when used together. This is evident in that the value of the induction period (t_2) for visible colour generated is slightly longer for the synergistic mixture than it is for the tin maleate alone. However some of the deleterious effects of the additives are also in evidence particularly at the higher temperature. For example the extents of gel and colour formation in the synergistic system is higher during the initial stage at 210°. The beneficial effects of the lubricating components of the synergistic mixture are particularly evident at the lower temperature, i.e. under conditions where the shearing forces might be expected to be more important. This is consistent with the greater beneficial effect of the lubricant, Wax E at 170° than at 210° (see Fig. 5).

The absence of measurable peroxide during the induction period in the SnM system is unexpected in view of the fact that considerable unsaturation is present in the polymer. The formation of peroxide appears to follow the end of the induction period which precedes the second stage of formation of unsaturation (Fig. 3) which is more extensively conjugated than the primary unsaturation as indicated by the formation of chromophores absorbing at 255, 288 and 337 nm and of visible colour from this point. This will result in an increasing concentration of methylene groups adjacent to conjugation and hence an increasing concentration of free radicals and hence of peroxides. However this does not explain the absence of mechano-chemically formed peroxide which is evident in unstabilized PVC and should be formed in parallel with the initial unsaturation. It has previously been suggested [8] that diakyl tin carboxylates may react with free radicals formed in the polymer by reaction (3).

$$R\cdot + R'_2Sn(OCOR'')_2 \rightarrow R\text{-}R' + R'Sn(OCOR'')_2 \qquad (3)$$

However this would not lead to the formation of initial unsaturation and must be discounted in the present case. It seems more likely that the presence of a conventional hindered phenolic antioxidant identified as a minor component ($\simeq 5\%$) in the tin stabilizer is involved in the elimination of the short chain reactions which lead to peroxide formation. This possibility is being investigated further.

CONCLUSIONS

It is concluded that the mechano-chemical processes leading to the formation of unsaturation and which occur during the first minute of processing can be reduced by the use of lubricants but that the latter may increase the rate of subsequent thermal oxidative reactions. A tin maleate stabilizer on the other hand appears actually to increase the severity of the mechano-chemical reaction but retards the second stage by removing allylic chlorine and conjugated unsaturation.

A synergistic mixture of these two types of additive combines the favourable influence of both giving a longer induction period to colour formation. However in some respects, for example, in the earlier formation of unsaturation and peroxides during the second stage, it shows a worse performance than the tin maleate alone.

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