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Aromatic 1,3,4-oxadiazoles as thermal stabilizers for rigid poly(vinyl chloride)

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Abstract

Several aromatic 1,3,4-oxadiazole derivatives have been investigated as thermal stabilizers for rigid poly(vinyl chloride) (PVC) at 180°C in air. Their stabilizing efficiencies are evaluated by measuring the rate of dehydrochlorination and the extent of discoloration of the degraded polymer. The results obtained show the greater stabilizing efficiency of the investigated compounds as compared with dibasic lead carbonate (DBLC), barium–cadmium–zinc stearate (Ba–Cd–Zn stearate) and n-octyltin mercaptide (n-OTM), which are commonly used industrial stabilizers. Their higher efficiencies are indicated not only by their longer induction periods during which no detectable amounts of hydrogen chloride gas are liberated, but also by their lower dehydrochlorination rates during the subsequent stages of degradation. The stabilizing efficiency of these compounds is influenced by the number of the 1,3,4-oxadiazole rings as well as by the introduction of electron donating substituents in the phenyl ring of the stabilizer molecule. This can be attributed to the replacement of the labile chlorine atoms on the polymer chains by more stable groups derived from the stabilizer. This substitution reaction proceeds most probably through an ionic mechanism. Moreover, stabilization with the investigated compounds results in an improvement in the extent of discoloration of the degraded PVC relative to the reference stabilizers. This may be attributed to the ability of these compounds to disrupt the formation of the conjugated double bonds which are responsible for discoloration. Combination of the investigated compounds with industrial stabilizers greatly improves the stabilizing efficiency which reaches its maximum at a molar ratio of oxadiazole stabilizer/reference stabilizer of 3:1. This synergism occurs due to the interaction between the residual investigated stabilizers with the reference metallic stabilizers' by-products, metal chlorides, thus protecting the polymer from the deleterious effect of these chlorides that accumulate when the metallic stabilizers are used alone.

Keywords: Poly(vinyl chloride); Thermal stabilizers; Dehydrochlorination rate

1. Introduction

Poly(vinyl chloride) (PVC) is a material of long standing and has enormous technical and economic importance. Its degradation during moulding or exploitation at high temperature still remains one of its main problems. This is usually demonstrated by the auto-catalytic dehydrochlorination reaction and discoloration of the polymer [1,2]. Degradation also causes a drastic change in the mechanical properties of the polymer accompanied with a decrease or an increase in molecular weight as a result of chain scission or cross-linking of the polymer molecules, respectively [3,4]. Thermal degradation occurs due to the presence of labile sites in the polymer chains, such as allyl chlorine [5–7], tertiary hydrogen and chlorine atoms [8], terminal end groups such as double bonds [9], oxygen-containing groups [10], peroxide residues [11,12], head-to-head structures [13] and the steric order of the monomer (the tacticity) [14,15]. This requires stabilization of the polymer for practically all technical applications. The stabilization adopted accordingly involves intervention with the dehydrochlorination process and reaction with the double bonds created on the backbone chains as a result of hydrogen chloride loss during degradation. A wide variety of stabilizers are used industrially to improve the thermal stability of the polymer. The commonly used stabilizers are usually basic lead salts [16–18] that can react with the evolved hydrogen chloride or substances that can exchange the labile functional groups in the backbone chains for other more stable substituents derived from the stabilizer; for example, metallic soaps [19–22], esters or mercaptides of dialkyltin [23–25] or materials whose stabilizing action is through intervention in the radical process of degradation

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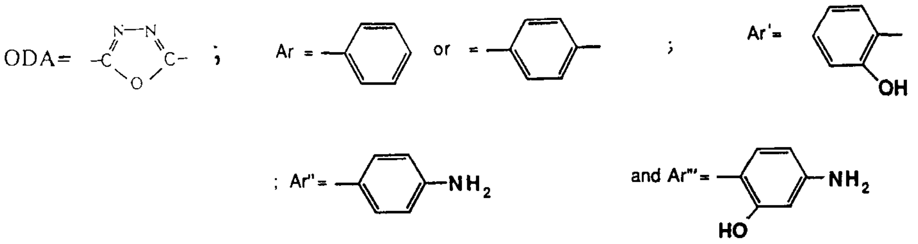
Table 1
Some characteristics of various aromatic 1,3,4-oxadiazole derivatives

Stabilizer code	Stabilizer structure	Melting point (°C)
I	Ar–ODA–Ar	281
II	Ar–ODA–Ar′	294
III	Ar–ODA–Ar″	308
IV	Ar–ODA–Ar‴	320
V	Ar–ODA–Ar–ODA–Ar	367
VI	Ar′–ODA–Ar–ODA–Ar′	392
VII	Ar″–ODA–Ar–ODA–Ar″	403
VIII	Ar‴–ODA–Ar–ODA–Ar‴	> 500



and effective absorption of the degradation products, such as quinone–tin polymers [26,27]. Moreover, the stabilizer may function by disruption of the conjugated systems, thus reducing the discoloration of the polymer and the defect sites (allylic sites) in its chains. Mercaptans are typical examples of these stabilizers [28].

However, irrespective of their stabilizing efficiencies, they suffer from the deleterious effect of their by-products, mostly metal chlorides, accumulated during the reaction of these stabilizers with the polymeric chains. These metal chlorides are considered as strong catalysts for the subsequent dehydrochlorination process, are responsible for the sudden blackening of certain formulations, and may present a serious environmental problem [29–31]. For this reason, stabilizers of an organic nature have been used recently for the thermal stabilization of PVC [32–37]. Aromatic 1,3,4-oxadiazole derivatives are organic compounds that possess in their structures many basic functional groups in addition to their highly conjugated systems. These desirable structures provide these compounds not only with the ability to intervene in the degradation process but also to act as strong hydrogen chloride absorbers, thus protecting the polymer from the deleterious effect of the acidic degradation products. Moreover, these compounds can withstand high temperature. Still another advantage of these compounds is their ability to be complexed with various metal ions after their transformation to the corresponding hydrazide derivatives [38,39]. This property allows these compounds to react with metal chlorides resulting as by-products from metallic stabilizers, thus preventing or at least minimizing their catalytic degradative action. For these reasons, it has been found of interest to investigate the possibility of using aromatic 1,3,4-oxadiazole derivatives as thermal stabilizers or co-stabilizers for rigid PVC.

2. Experimental procedures

2.1. Materials

PVC (suspension) from Huls Company (Germany) with a K value of 70; n-octyltin mercaptide (n-OTM) from Ameria Company for PVC Manufacturing (Alexandria, Egypt); dibasic lead carbonate (DBLC) from the National Lead Company (Germany); and barium–cadmium–zinc stearate complex (Ba–Cd–Zn stearate) from G. Siegle and Co. (Siegle-Farben, Germany) were used for this investigation.

2.2. Preparation of the stabilizers

Various aromatic 1,3,4-oxadiazole derivatives listed in Table 1 were prepared according to the method described by Frost et al. [40]. They were obtained from the corresponding hydrazides that were prepared in previous work [36], via cyclodehydration. The preparations were carried out by mixing the hydrazide compounds with 10 times their weights of polyphosphoric acid (84.5% P_2O_5). The resulting mixtures were heated slowly to 200–220°C with stirring. They were then allowed to cool to about 120°C and precipitated into dilute sodium carbonate solution. The solid products obtained were filtered, washed repeatedly with water, and recrystallized from *N*,*N*-dimethyl acetamide. The results of their elemental analyses and IR spectra (Table 2) agreed well and confirmed the representative structures of these compounds (Table 1).

2.3. Preparation of PVC samples for degradation

The PVC samples were prepared according to the

Table 2
Elemental anlyses and main IR absorption peaks of various 1,3,4-oxadiazole derivatives

Stabilizer code	Elemental analyses (%)[a]				Main IR peaks (cm^{-1})		
	C	H	N	O	> C=N−	=C−O−	$-NH_2$ or/and −OH
I	75.70 (75.68)	4.45 (4.50)	12.57 (12.61)	7.28 (7.21)	1620	1020	−
II	70.49 (70.59)	4.24 (4.20)	11.73 (11.76)	13.54 (13.45)	1620	1020	3350
III	71.01 (70.89)	4.59 (4.64)	17.59 (17.72)	6.81 (6.75)	1620	1020	3250
IV	66.51 (66.40)	4.31 (4.35)	16.68 (16.60)	12.50 (12.65)	1620	1020	3400
V	72.19 (72.13)	3.79 (3.83)	15.39 (15.30)	8.63 (8.74)	1620	1020	−
VI	66.16 (66.17)	3.78 (3.76)	14.07 (14.04)	15.99 (16.04)	1620	1020	3350
VII	66.73 (66.67)	4.01 (4.04)	21.18 (21.21)	8.08 (8.08)	1620	1020	3250
VIII	61.71 (61.68)	3.72 (3.74)	19.57 (19.63)	15.00 (14.95)	1620	1020	3400

[a] The calculated elemental analyses are given in parentheses.

following:

Material	Part by weight
PVC	100
Thermal stabilizer	10 mmol

The ingredients were mixed thoroughly in a mortar, and 0.2 g of the resulting fine powder was used for the investigation.

2.4. Method of evaluating the stabilizing efficiency

Evaluation of the stabilizing efficiency was carried out by measuring the dehydrochlorination rate using continuous potentiometric determination of the evolved hydrogen chloride gas at 180°C in air. A detailed description of this method is given elsewhere [41]. A digital pH meter (potentiometer) of the type CG 822 (Schott Gerade GmbH, Germany) of accuracy of 1 digit = 1 mV was used. It was connected to a silver electrode and a reference saturated calomel electrode for the potentiometric measurements. The extent of discoloration of the degraded polymer samples was measured colorimetrically at λ = 400 nm as a function of the degradation time. A Perkin-Elmer UV/visible spectrophotometer of the type Lambda 3 (Germany) was used in this study. IR spectra were recorded on a Shimadzu Fourier transform infra-red spectrophotometer (FTIR 4200) in the range 4000–600 cm^{-1} at 25°C.

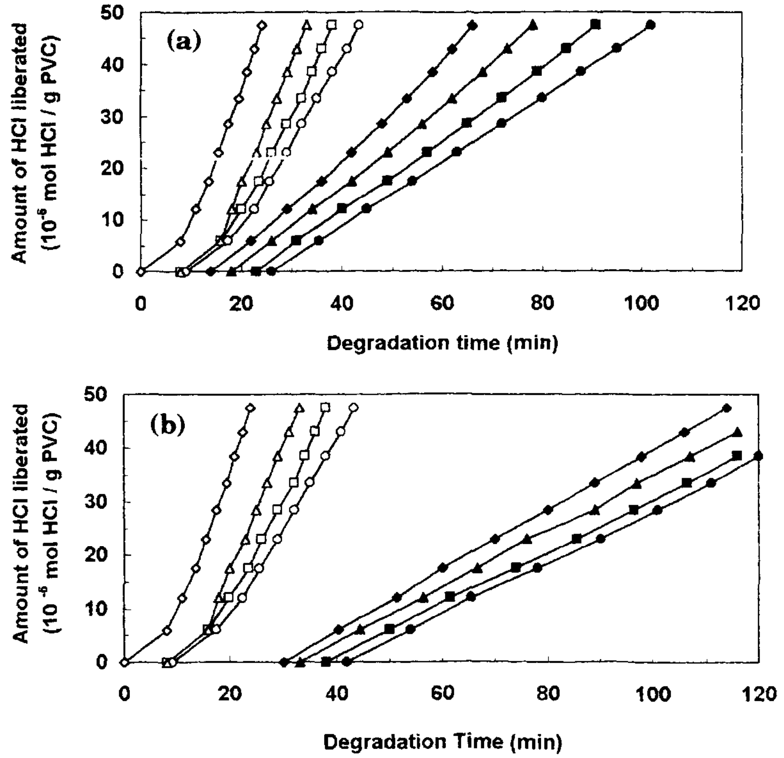


Fig. 1. Rate of dehydrochlorination of rigid PVC at 180°C in air in the presence of various aromatic 1,3,4-oxadiazole derivatives and reference stabilizers. All the stabilizers were used in concentrations of 10 mmol/100 g PVC: (a) (◇) blank, (△) DBLC, (□) Ba–Cd–Zn stearate, (○) n-OTM, (◆) I, (▲) II, (■) III, (●) IV; (b) (◇) blank, (△) DBLC, (□) Ba–Cd–Zn stearate, (○) n-OTM, (◆) V, (▲) VI, (■) VII, (●) VIII.

Table 3
Induction period (T_s) dependence on stabilizer type for thermally degraded rigid PVC at 180°C in air

Stabilizer code	T_s (min)	Stabilizer code	T_s (min)
Blank	0	III	23
Ba–Cd–Zn stearate	8	IV	26
DBLC	8	V	30
n-OTM	9	VI	33
I	14	VII	38
II	18	VIII	42

3. Results and discussion

3.1. Stabilization of thermally degraded rigid PVC using various aromatic 1,3,4-oxadiazole derivatives

Results of dehydrochlorination of rigid PVC stabilized by various aromatic 1,3,4-oxadiazole derivatives against thermal degradation effected at 180°C in air, are represented in Fig. 1. The results of the non-stabilized blank sample as well as that of the samples stabilized by Ba–Cd–Zn stearate, DBLC and n-OTM industrial stabilizers are also given for comparison. For all experiments the stabilizers were used at a concentration of 10 mmol/100 g PVC, and the results given represent the average of three comparable experiments for each stabilizer.

It can be seen from this figure that the investigated compounds exhibit a greater stabilizing efficiency compared to that of the industrially used stabilizers. The greater efficiency is illustrated not only by well defined induction periods (T_s) during which no detectable amounts of hydrogen chloride gas are liberated (Table 3), but also by lower rates of dehydrochlorination during the subsequent stages of degradation reaction. The greater efficiency is so well pronounced that the length of the induction period (T_s) in case of derivative VIII exceeds by more than four times that obtained when any one of the industrial stabilizers was used. The results also show how that T_s and the rate of dehydrochlorination are strongly affected both by the type of substituents in the phenyl ring (–OH, $-NH_2$ groups) and the number of the 1,3,4-oxadiazole rings of the stabilizer molecule. The results reveal that the compounds having two 1,3,4-oxadiazole rings show higher values of T_s relative to those containing only one. The introduction of –OH or/and $-NH_2$ groups into the phenyl rings of the stabilizer results in an appreciable improvement in both T_s and the rate of dehydrochlorination. This fact confirms the important role played by both the oxadiazole rings and the substituents in the phenyl rings of the stabilizer in the stabilization

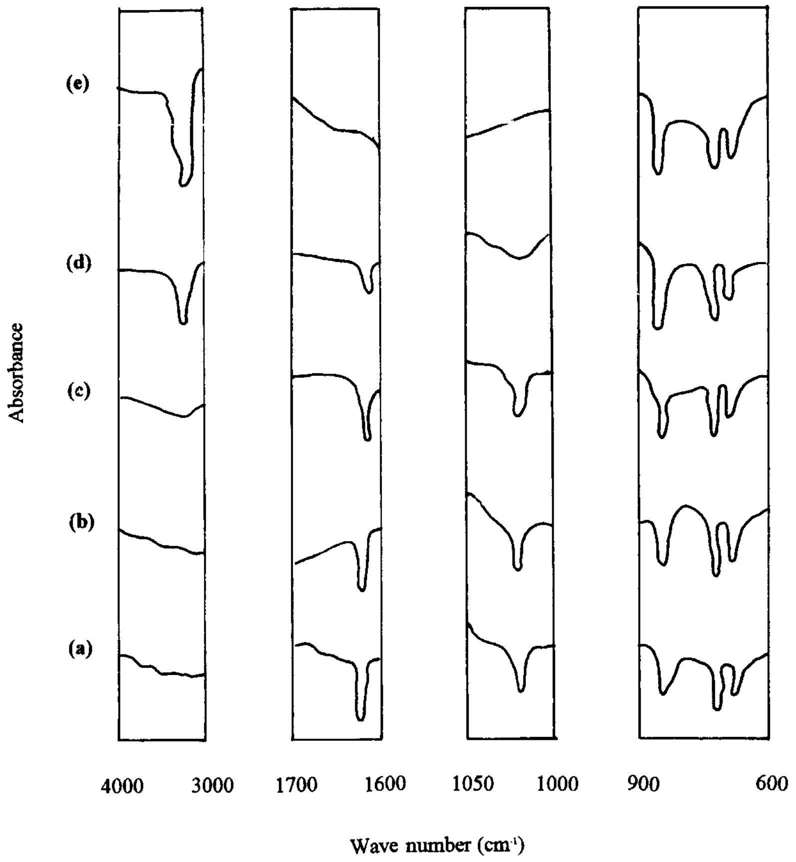
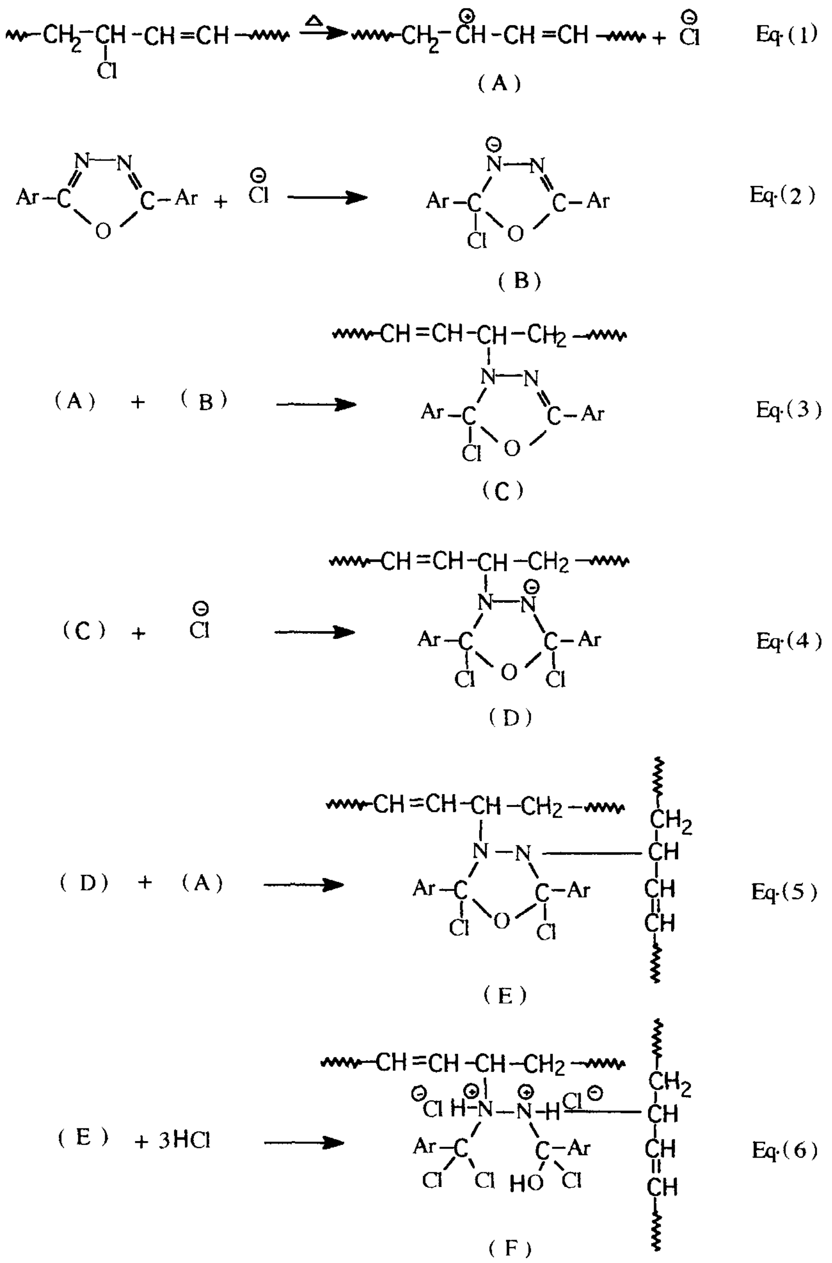


Fig. 2. Variation of IR spectra of thermally degraded rigid PVC at 180°C in air in the presence of stabilizer I as a function of degradation time: (a) 0 min; (b) 10 min; (c) 30 min; (d) 50 min; (e) 70 min.

mechanism. Moreover, the greater stabilizing efficiency of the investigated compounds in relation to the reference stabilizers implies that the mechanism of stabilization exhibited by them greatly differs from those of the reference stabilizers.

A mechanism for the stabilizing action of the oxadiazole derivatives, based on the aforementioned results, implies that the ability of the oxadiazole molecule to be incorporated into the body of the polymeric chain is to be expected and factors favouring this ability will accordingly lead to better efficiencies. This has been experimentally proved based on the following observations:

1. When a stream of hydrogen chloride gas is allowed to pass through the stabilizer I at 180°C for 30 min, the IR spectrum of the stabilizer I after treatment was found to be identical to that of the original non-treated sample. Further, this result has been confirmed by the absence of chlorine on analyzing the treated material. This implies that oxadiazole compound is not able to react with hydrogen chloride gas and consequently its high stabilizing efficiency cannot be attributed to a unimolecular mechanism of degradation and stabilization.
2. Another experiment was performed to examine the ability of the derivative to act as a radical trap. For this purpose, the oxadiazole derivative I in carbon tetrachloride was subjected to photolysis for 2 h using a low pressure UV lamp. A catalytic amount of benzophenone was added to enhance the radical decomposition of the carbon tetrachloride. No change in the IR spectrum



of the irradiated sample was observed and the elemental analysis of this sample was found to be free from chlorine atoms. This illustrates that the oxadiazole compound cannot be attacked by a chlorine atom and consequently its stabilizing power cannot be attributed to a radical mechanism of degradation and stabilization.

3. The elemental analyses of the PVC in the presence of various investigated derivatives during the course of degradation before and after the induction period and after extensive washing to remove any residual stabilizer (unreacted stabilizer) have shown that nitrogen is present in the polymeric material. This indicates that the stabilizer molecule, or at least a part of it, is chemically bonded to the degraded polymeric chains during the stabilization process, and that the stabilizing efficiency is at least partly due to the ability of the oxadiazole stabilizer to be incorporated into the polymeric chains. On the other hand, the elemental analyses showed the presence of chlorine in the extracted residual stabilizers.
4. The polymer undergoes very slight cross-linking either during or after the induction period as evidenced by the incomplete solubility of the degraded polymer in any of the solvents used.

Accordingly, The most probable mechanism that might account for the above-mentioned findings could be depicted as follows:

Thus, while the mechanism of thermal degradation of PVC could be explained on the basis of the involvement of either radical or ionic intermediates, the latter mechanism seems to be more favourable in the presence of the investigated material in view of its polar nature. Accordingly, reactions (1)–(3) represent some sort of elimination–addition reaction in which the chloride anion split from the labile site on the polymeric chain is linked to the oxadiazole molecule at one of its electron-deficient sites (> C=N– group). The electron deficiency of this group is attributed to the electron withdrawing nature of the adjacent phenyl ring. The above process is greatly favoured by the resulting highly resonance stabilized oxadiazole anion. The latter will be attracted toward the positively charged position created on the polymeric chain, thus leading to the chemical incorporation of oxadiazole residue into the polymeric matrix. The net result of these two steps is the replacement of the labile chlorine atom by a relatively more stable oxadiazole moiety. An experimental proof supporting this mechanism comes from the presence of nitrogen in the elemental analysis of the degraded polymer. Similarly, an elimination–addition reaction is also possible between the labile chlorine anion and the other unsaturated site in the oxadiazole residue that is already attached to the polymeric chain (reactions (4) and (5)). This might explain the very slight cross-linking of the degraded polymer as detected by the presence of fine insoluble particles. Thus, while the unsaturated centres of the oxadiazole are involved in the replacement of the labile group, the compound still possesses a stabilizing activity—it being a hydrogen chloride absorber through its –C–O– linkage as well as its various basic groups which can react with up to three molecules of liberated hydrogen chloride (reaction (6)). The results of all the above reactions, which involve both the addition of the oxadiazole to the polymer chains as well as the absorption of the hydrogen chloride liberated by the stabilizer moiety, is responsible for the long T_s and the lower rate of dehydrochlorination. It seems probable that the reaction with the unsaturated sites resulting in incorporation of oxadiazole into the polymeric chain precedes the addition of any liberated hydrogen chloride to the already attached stabilizer moiety. This mechanism can find experimental support from recording the IR spectra of PVC samples stabilized with derivative I and thermally degraded at 180°C in air for various time intervals (0, 10, 30, 50 and 70 min). In these cases, the stabilizer I was used in a much higher concentration (100 mmol/100 g PVC) than commonly used in order to facilitate the detection of any changes in the resulting spectra. The resulting degraded samples were repeatedly washed with hot *N*,*N*-dimethyl acetamide, to remove the unreacted stabilizer, before measuring the IR spectra. The changes of the IR spectra of these samples are represented in Fig. 2. The IR spectrum of the derivative I alone shows two main characteristic absorption bands at 1620 and 1020 cm^{-1} which correspond to > C=N– and =C–O– groups, respectively, as listed in Table 2 and shown in Fig. 2(a). However, IR spectra of PVC samples at subsequent stages of degradation (Fig. 2(b–e)) showed the following changes:

1. The absorption band of the > C=N– group gradually disappeared as the degradation time was increased together with a slight shift in its position to shorter wavelength (from 1620 to 1610 cm^{-1}). This indicated a loss of carbon–nitrogen double bond character during its participation in the stabilization process.
2. The band corresponding to –O–C= (at 1020 cm^{-1}) firstly did not change up to 30 min of degradation, but had disappeared completely when the degradation time reached 70 min indicating participation of this group in the later stages of the stabilization process.
3. The appearance of a new absorption band at 3250 cm^{-1}, at later stages of degradation, corresponds to the > NH group which may result from protonation of the –N–C group, in addition to the bands at 690, 720 and 850 cm^{-1} from the beginning of the degradation process, which confirm the presence of the aromatic moiety within the polymeric chains.

Moreover, the stabilizing efficiency increases as a function of oxadiazole ring content of the stabilizer molecule. This is further evidence indicating the participation of the oxadiazole moiety in the stabilization process. On the other hand, aromatic oxadiazoles having electron rich substituents (–NH_2 and/or –OH groups), which can

Table 4
Induction period (min) as a function of stabilizer concentration

Stabilizer code	Stabilizer concentration (mmol/100 g PVC)		
	2.5	5	10
IV	9	17	26
VIII	22	30	42

donate electrons towards the carbon–nitrogen double bond (–N=C <) of the oxadiazole ring, showed high stabilizing efficiency relative to that of the unsubstituted one. An experimental proof supporting this conclusion can be seen in the greater efficiency of the amino derivative relative to that of the hydroxy derivative. This is in accordance with the greater electron donating power of the $-NH_2$ group relative to the –OH group. The enhanced efficiency of the amino derivative can also be related to another two reasons. First, the presence of the amino group in position 4 in the phenyl ring may make its electron donation towards the carbon–nitrogen double bond proceed to a greater extent and to be much easier. Second is ability of the amino derivative to act as a hydrogen chloride absorber based on its basic character.

The great improvement in the stabilization of PVC against thermal degradation using the oxadiazole derivatives as detected by the longer induction period during which no detectable changes in the polymer are observed, has led to the conclusion that comparable stabilizing efficiencies could be observed if the oxadiazoles are used in concentrations lower than those commonly used in industry. For this purpose, the study was extended to determine the lowest amount of either oxadiazole derivative IV or VIII which can provide stabilizing power comparable with the industrially used stabilizers. The details of the experiment are given in Table 4 and the results are illustrated in Fig. 3. The results reveal that a comparable stabilizing effect could be achieved when the oxadiazole IV is used at a concentration of only a quarter of that of the three industrially used reference stabilizers. The greater efficiency of the oxadiazole derivatives even at low concentration is most probably due not only to their possession of various centres of reactivity that can act as traps for the ion species resulting during the degradation process, but also due to their ability to react with the evolved hydrogen chloride gas. Further, it can be noted that T_s decreases at a relatively constant dehydrochlorination rate. This gives strong evidence for the role played by both the oxadiazole ring as well as the substituents in the phenyl ring of the stabilizer in the stabilization process.

3.2. The oxadiazole derivatives and discoloration of thermally degraded rigid PVC

The time dependence of the extent of discoloration of rigid PVC samples treated with oxadiazole derivatives I, IV and VIII when heated at 180°C in air, as compared

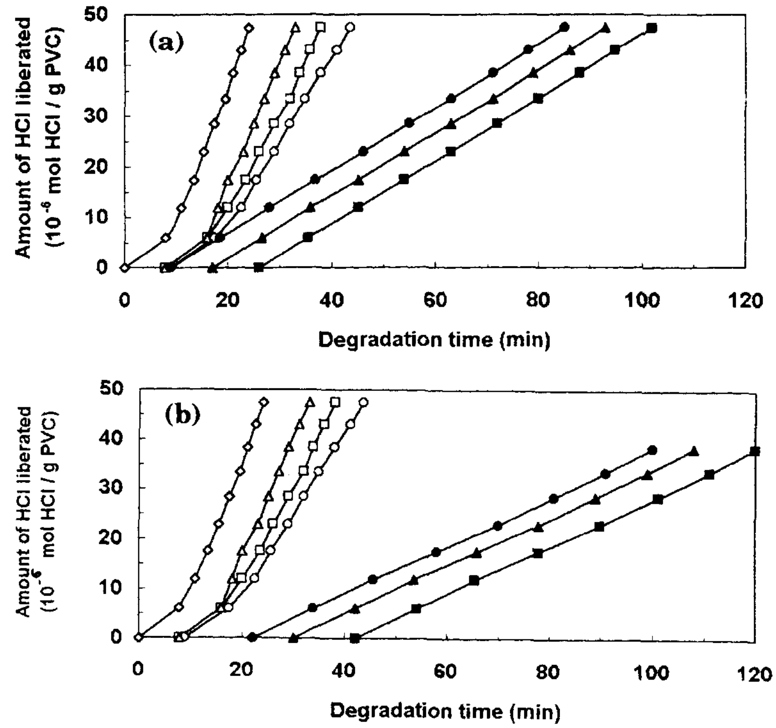


Fig. 3. Effect of oxadiazole stabilizers IV and VIII concentration on the rate of dehydrochlorination of thermally degraded rigid PVC at 180°C in air: (a) (◇) blank, (△) 10 mmol/100 g PVC of DBLC, (□) 10 mmol/100 g PVC of Ba–Cd–Zn stearate, (○) 10 mmol/100 g PVC of n-OTM, (●) 2.5 mmol/100 g PVC of IV, (▲) 5 mmol/100 g PVC of IV, (■) 10 mmol/100 g PVC of IV; (b) (◇) blank, (△) 10 mmol/100 g PVC of DBLC, (□) 10 mmol/100 g PVC of Ba–Cd–Zn stearate, (○) 10 mmol/100 g PVC of n-OTM, (●) 2.5 mmol/100 g PVC of VIII, (▲) 5 mmol/100 g PVC of VIII, (■) 10 mmol/100 g PVC of VIII.

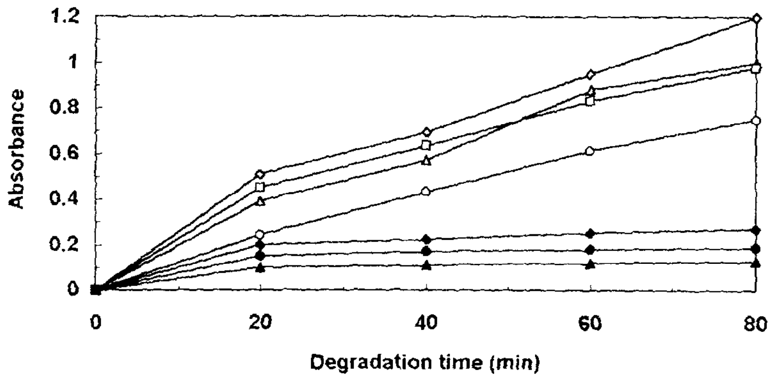


Fig. 4. Absorbance as a function of thermal degradation periods of rigid PVC. The samples had been heated at 180°C in air, and treated with 10 mmol/100 g PVC of various stabilizers. The sample concentrations were 100 mg in 10 ml tetrahydrofuran and the absorbance was measured at λ = 400 nm: (◇) blank; (△) DBLC; (□) Ba–Cd–Zn stearate; (○) n-OTM; (♦) I; (●) IV; (▲) VIII.

with the blank sample and samples stabilized with DBLC, Ba–Cd–Zn stearate and n-OTM reference stabilizers, is shown in Fig. 4. The extent of discoloration was determined colorimetrically by measuring the absorbance at λ = 400 nm for the various samples as a function of the degradation time. The results reveal that the samples treated with oxadiazole derivatives showed a better extent of discoloration than those treated with the references

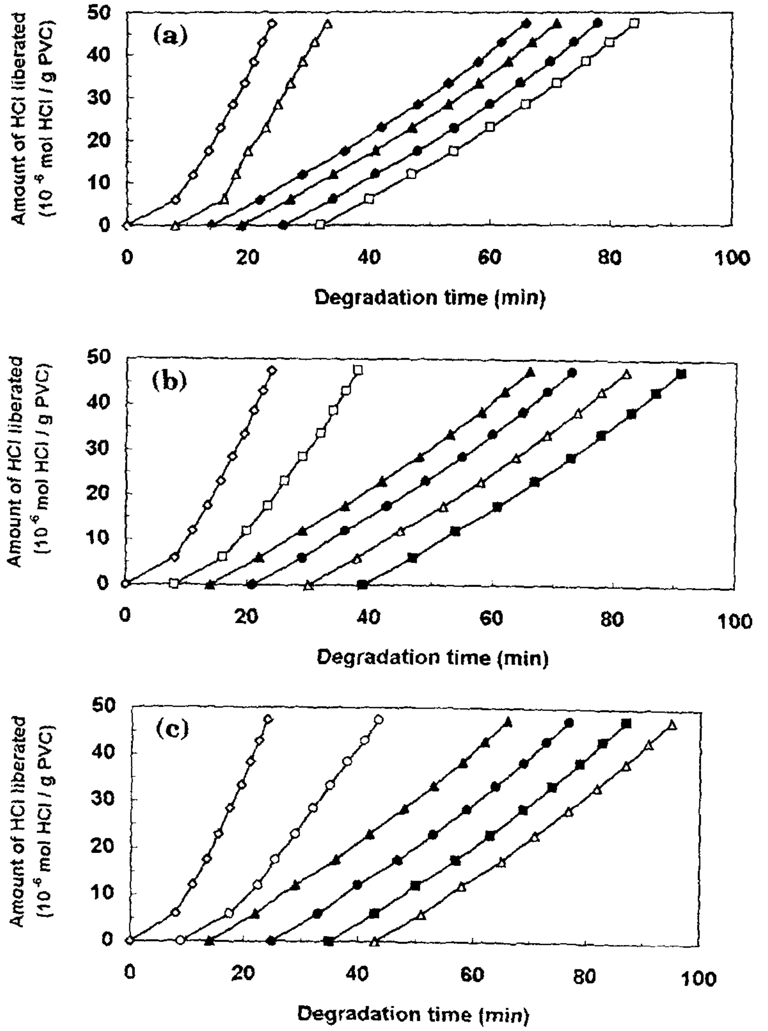


Fig. 5. Effect of mixed stabilizers (I and DBLC), (I and BA–Cd–Zn Stearate) and (I and n-OTM) on the rate of dehydrochlorination of thermally degraded rigid PVC at 180°C in air. The overall mixed stabilizers were kept constant at 10 mmol/100 g PVC: (a) (◇) blank, (△) 100% DBLC, (♦) 100% I, (▲) 25% I, (●) 50% I, (□) 75% I; (b) (◇) blank, (□) 100% Ba–Cd–Zn stearate, (▲) 100% I, (●) 25% I, (△) 50% I, (■) 75% I; (c) (◇) blank, (○) 100% n-OTM, (▲) 100% I, (●) 25% I, (■) 50% I, (△) 75% I.

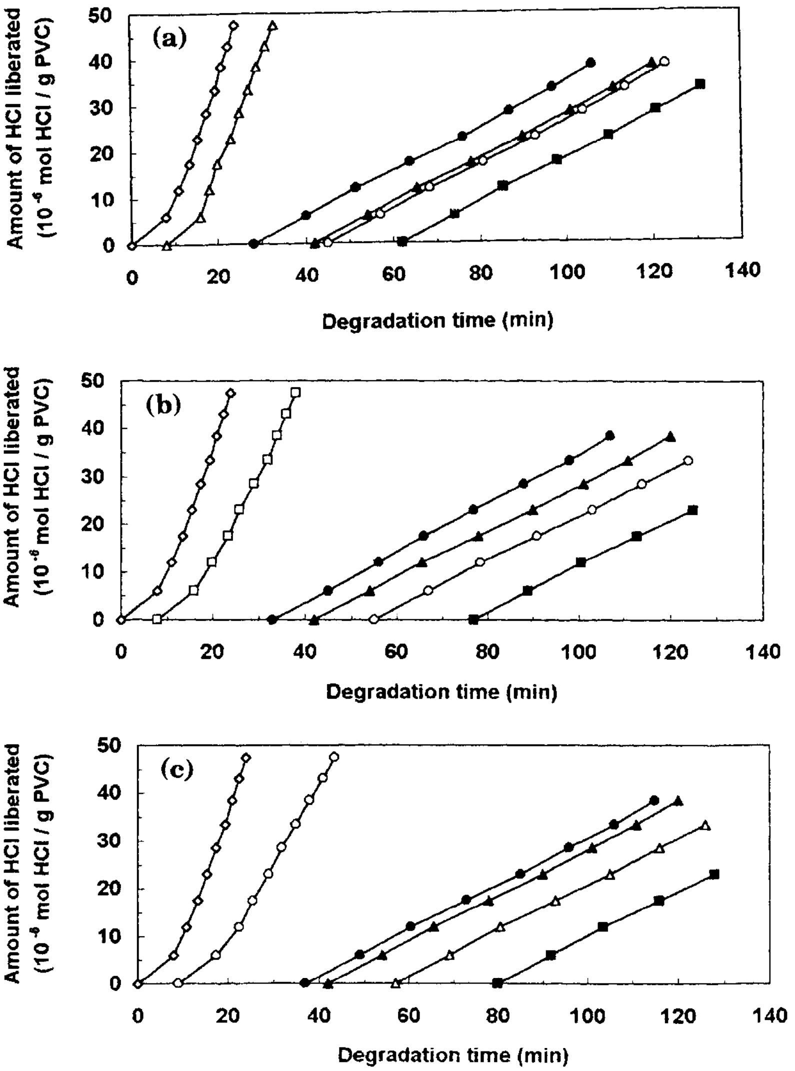


Fig. 6. Effect of mixed stabilizers (VIII and DBLC) (VIII and Ba–Cd–Zn Stearate) and (VIII and n-OTM) on the rate of dehydrochlorination of thermally degraded rigid PVC at 180°C in air. The overall mixed stabilizers were kept constant at 10 mmol/100 g PVC: (a) (◇) blank, (△) 100% DBLC, (▲) 100% VIII, (●) 25% VIII, (○) 50% VIII, (■) 75% VIII; (b) (◇) blank, (□) 100% Ba–Cd–Zn stearate, (▲) 100% VIII, (●) 25% VIII, (○) 50% VIII, (■) 75% VIII; (c) (◇) blank, (○) 100% n-OTM, (▲) 100% VIII, (●) 25% VIII, (△) 50% VIII, (■) 75% VIII.

stabilizers. This reflects the greater stabilizing efficiency of the investigated stabilizers through the replacement of the labile chlorine by a more thermally stable moiety which disrupts the formation of the conjugated double bonds that are responsible for discoloration.

3.3. Stabilization of thermally degraded rigid PVC using mixed stabilizers

It was found above that the stabilizing mechanism of various oxadiazole derivatives is performed through

Table 5
Effect of mixing either I or VIII with the reference stabilizers on T_s values of thermally degraded rigid PVC at 180°C in air

Molar ratio	T_s (min)					
	I/DBLC	I/Ba–Cd–Zn stearate	I/n-OTM	VIII/DBLC	VIII/Ba–Cd–Zn stearate	VIII/n-OTM
100/0	14	14	14	42	42	42
75/25	32	39	43	62	77	80
50/50	26	30	35	45	55	57
25/75	19	21	25	28	33	37
0/100	8	8	9	8	8	9

Table 6
Effect of mixing either I or VIII with the reference stabilizers on the dicoloration of thermally degraded rigid PVC at 180°C in air for 80 min

Molar ratio	Absorbance at $\lambda = 400$ nm					
	I/DBLC	I/Ba–Cd–Zn stearate	I/n-OTM	VIII/DBLC	VIII/Ba–Cd–Zn stearate	VIII/n-OTM
100/0	0.27	0.27	0.27	0.13	0.13	0.13
75/25	0.21	0.19	0.18	0.11	0.09	0.07
50/50	0.38	0.26	0.24	0.28	0.19	0.17
25/75	0.61	0.42	0.38	0.36	0.25	0.29
0/100	1.00	0.98	0.75	1.00	0.98	0.75

replacement of the unstable allyl chlorine with a relatively stable stabilizer moiety and through absorption of the evolved hydrogen chloride gas. However, almost all the commonly known stabilizers chosen in the present study as references operate either through neutralization of the evolved hydrogen chloride gas (DBLC) or through replacing the weakly bonded allyl chlorine atom by a substituent which is of greater stability (as in the case of soap and tin stabilizers). Accordingly, it became of interest to investigate the effect on the efficiency of stabilization of mixing the stabilizers under investigation with those used in industry. Stabilizers I and VIII exhibiting lowest and highest T_s values were selected for this purpose. Mixing was effected in the range 0–100% of the oxadiazole derivative relative to the reference stabilizers used. The overall mixed stabilizer concentration was kept constant at 10 mmol/100 g PVC and the results represent the average of three comparable experiments for each stabilizer mixture. The results of the dehydrochlorination of thermally degraded PVC at 180°C in air in the presence of the mixed stabilizers are shown in Figs 5 and 6. The induction periods of the stabilizer combinations are given in Table 5. The results clearly reveal the existence of a true synergistic effect resulting from the combination of oxadiazole stabilizer with any of the investigated reference stabilizers. The maximum synergism was achieved when the oxadiazole (I or VIII) and either DBLC, Ba–Cd–Zn stearate or n-OTM were mixed in a 3:1 molar ratio.

In order to find an explanation for the well-defined synergistic action shown when the oxadiazole is mixed with reference stabilizers, two experiments were performed. First, heating a mixture of 3:1 oxadiazole and reference stabilizer at 180°C in air, followed by fractional crystallization, shows no change in the melting point of the oxadiazole derivative and no detectable loss in its mole fraction, which indicates that there is no chemical reaction between the oxadiazole and either of the reference stabilizers. The second, comparing the UV spectra of the mixed stabilizers taken in 3:1 molar ratio with those of pure components, shows the absence of any interaction between the components of the mixtures as no shift was seen in the UV bands characteristic of the oxadiazole derivatives. Accordingly, it seems that the synergistic action attained results from the different mechanisms by which the oxadiazole and the reference stabilizers work.

This fact is experimentally supported by observing the rate of dehydrochlorination in all cases, at various molar ratios of the components of the mixed stabilizers which are comparable with those characteristics for the stabilizer I and VIII rather than the reference ones. This indicates that aromatic oxadiazoles and the reference stabilizers act separately through replacement of the labile chlorine and reaction with the liberated hydrogen chloride gas. The improvement of the stabilizing efficiency of the reference metallic stabilizers through their mixing with oxadiazole derivative may be attributed to the possibility for the latter, at subsequent stages of degradation, to react with the accumulated metal chlorides ($ZnCl_2$, $CdCl_2$, $PbCl_2$ and $SnCl_2$), produced as by-products from the reference stabilizers, to form in situ stabilizer complexes of higher stabilizing efficiency. Thus, it is hoped through these combinations not only to eliminate the deleterious effect of the metal chlorides, but also to obtain the possibility of their transformation into additional useful stabilizers.

3.4. Effect of mixed stabilizers on the degree of discoloration for thermally degraded rigid PVC

The effects of mixing stabilizers I or VIII with either DBLC, Ba–Cd–Zn stearate or n-OTM in various molar ratios, ranging from 0 to 100%, on the extent of discoloration of thermally degraded rigid PVC at 180°C in air, are represented in Table 6. All the samples were heated for a fixed time period of 80 min. The results reveal that all the mixed stabilizers show a lower extent of discoloration than the reference stabilizers, rather than the investigated stabilizers, when they are used separately. In all cases, a 3:1 molar ratio between the oxadiazole and the reference stabilizers imparts the lowest degree of discoloration and consequently the best colour stability. This result indicates the synergistic effect between their modes of action.

4. Conclusion

The above results and discussion lead to the following general conclusions:

1. Aromatic 1,3,4-oxadiazole derivatives are efficient thermal stabilizers for rigid PVC even if they are added in lower concentration relative to the commonly used reference stabilizers such as DBLC, Ba–Cd–Zn stearate or n-OTM.
2. The stabilizing efficiency of the oxadiazole derivatives is attributed to the ability of these compounds to replace the labile chlorine by a relatively more thermally stable aromatic oxadiazole moiety and to absorb the liberated hydrogen chloride gas.
3. The induction period, observed during the initial stages of degradation, is found to be strongly influenced by both the number of oxadiazole rings and the substituents in the phenyl ring of the stabilizer molecule.
4. The rate of dehydrochlorination of PVC, at subsequent stages of degradation, is substantially retarded by the basic groups of the stabilizers.
5. The investigated stabilizers lower the extent of discoloration of the degraded PVC samples by disrupting the conjugated double bond sequences formed in the polymeric chains.
6. Mixing the oxadiazole stabilizers with any of the industrially used stabilizers leads to a remarkable improvement both in the T_s value and in lowering the degree of discoloration, reaching a maximum at a 3:1 molar ratio of oxadiazole to reference stabilizer.

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