Synergistic Stabilizing Effect of Combination of Maleimido Phenyl Thiourea Derivatives and Some Commercial Stabilizers against Thermal Degradation of PVC

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Abstract: *Four novel antimicrobial maleimido phenyl thiourea stabilizers **1-4** were synthesized from N-[4-(chlorocarbonyl) phenyl] maleimide with phenyl thiourea and its derivatives (p-methyl, o-chloro and p-carboxy). The effect of mixing maleimido phenyl thiourea stabilizer **2** with each of the reference stabilizers: dibasic lead carbonate (DBLC), cadmium-barium-zinc stearate (Cd-Ba-Zn stearate) or n-octyltinmercaptide (n-OTM) on the stabilization efficiency against thermal degradation of rigid PVC at 180 ^{o}C, in air, has been investigated. Mixing was effected in the range of 0-100 wt% of stabilizer **2**relative to each of the reference stabilizers. The stabilizing efficiency was evaluated by measuring the length of the thermal stability period (Ts), the period during which no detectable amounts of hydrogen chloride gas could be observed, and also from the rate of dehydrochlorination as measured by continuous potentiometric determination on the one hand, and the extent of discoloration of the degraded polymer samples on the other. The results show a true synergistic effect from the combination of stabilizer **2** with any of the reference stabilizers. Mixing of the stabilizers improves the Ts values, decreases the rate of dehydrochlorination, and lowers the extent of discoloration of the polymer. The maximum synergism was attained when the stabilizer **2** is mixed with either of the three reference stabilizers in equivalent weight ratio (50%/50%). The observed synergism may be attributed to the different mechanisms by which the investigated and the reference stabilizers work.*

Keywords: *PVC; Mixed stabilizers; Dehydrochlorination rate; Discoloration degree; Synergistic effect*

1. INTRODUCTION

Poly (vinyl chloride), PVC, is a material of enormous technical and economic importance. It stands second in the world after polyethylene concerning the production and consumption of a synthetic material. Its extensive autocatalytic dehydrochlorination with the subsequent formation of conjugated double bonds upon exposure to high temperature during its molding or use still remains one of its main problems [1]. This results in an unacceptable discoloration of the polymer and a drastic change in its physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain scission or cross linking, respectively, which can reduce the useful life of its articles [2-4].It is assumed that various defect sites in the polymer chains are responsible for this instability. Possible defect structures in PVC are branching, chloroallyl groups, end groups, oxygen containing groups, head to-head structures and the stereo order of the monomer units (tacticity) [5-10].

In general, the great commercial importance of PVC can be attributed to the development of effective means of stabilization. The thermal stabilizers commonly in use for the stabilization of PVC are either basic salts [11] which can react with the evolved hydrogen chloride gas, thus retarding the deleterious catalytic action of the eliminated hydrogen chloride [12], metallic soaps [13] and esters or mercaptides of dialkyltin [14] that can exchange the labile chlorine in the backbone by other more stable ester or mercaptide group derived from the stabilizer. Moreover,

stabilizers of an organic nature have also been developed to avoid the deleterious effect of the metal chlorides, by-products of metallic stabilizers, accumulated during the reaction of organometallic stabilizers with the PVC [15-18]. These metal chlorides are considered as strong catalysts for the subsequent dehydrochlorination process, are responsible for sudden blackening of certain formulations and may present a serious environmental problem [19,20].

On the otherhand, PVC products for certain applications in the fields of construction, food package, decoration, medicine (e. g. for the fabrication of indwelling catheters in the hospital care) and commodities such as construction tubing, films, toys, wallpaper, … etc, cannot avoid smirching with microbes during their daily usage. For this, recently, a new trend has been established based on the use of fully organic stabilizers of antimicrobial nature to obtain thermally stable antimicrobial PVC composites [21-23].

In our previous work [23], we have suggested that the stabilizing action of various antimicrobial maleimido phenyl thiourea stabilizers is due to a radical mechanism which disrupts the radical chain degradation process of the polymer through blocking the odd electron sites created on the PVC chains. However, almost all the commonly known stabilizers chosen in this study as references function through either neutralization of the evolved hydrogen chloride gas (the case of basic salts such as dibasic lead carbonate, DBLC), or through replacing the weakly bonded chlorine atoms by substituents which are of greater stability (the case of both soap and organotin stabilizer such as cadmium-barium-zinc stearate complex, Cd-Ba-Zn stearate, and n-octyltinmercaptide, n-OTM, respectively). Accordingly, it became of interest to investigate the effect of mixing maleimido phenyl thiourea stabilizer **2** (which seems to have a relatively higher stabilizing efficiency than other maleimido phenyl thiourea stabilizers **1**, **3** and **4**) together with those used in industry on the efficiency of thermal stabilization of PVC.

2. EXPERIMENTAL

2.1. Materials

The PVC (suspension) usedin this study was additive free, with a K value of 70 and was supplied by Hüls Co. (Frankfurt, Germany). Cadmium-barium-zinc stearate complex (Cd-Ba-Zn stearate) obtained from G. Siegle and Co. (Stuttgart, Germany), n-octyltinmercaptide (n-OTM) obtained from America Company for PVC manufacturing (Alexandria, Egypt), dibasic lead carbonate (DBLC) obtained from the National lead Co. (Darmstadt, Germany), p-amino benzoic acid, aniline and potassium thiocyanate obtained from Oxford(Mumbai, India), p-toluidine, and o-choloroaniline obtained from Schuchard(München, Germany) were also used.. N-[4-(chlorocarbonyl) phenyl] maleimide was synthesized according to the method described by Oishi and Fujimoto [24].

2.2. Preparation of Maleimido Phenyl Thiourea and its Derivatives

Four maleimido phenyl thiourea stabilizers **1-4** were prepared according to the method described in our previous work [23] as shown in Scheme 1. Briefly, an equimolar amounts of dry potassium thiocyanate and N-[4-(chlorocarbonyl)phenyl)maleimide were dissolved separately in least amount of dry acetone and cooled in ice-salt bath at 0-5 ℃ for 15 min. After complete dissolution, the N-[4-(chlorocarbonyl)phenyl)maleimide solution was added drop wisely to potassium thiocyanate solution with constant stirring for 1hr. The white precipitate of the formed ammonium chloride was removed by filtration and the filtrate was added gradually to the dry acetone solution of appropriate amount of the corresponding amine with stirring for 1 hr. The reaction mixture was poured on crushed ice and the resulting crude was filtered, dried in oven at 80 ℃ and finally recrystallized from boiling water [25].

Derivative no.	1	2	3	4
X	H	H	Cl	H
Y	H	CH$_3$	H	COOH
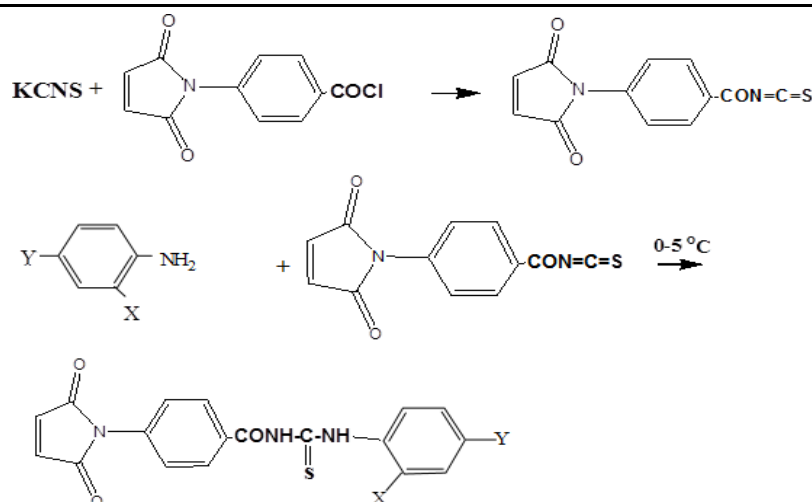
Scheme1. *Synthesis of maleimido phenyl thiourea derivatives.*

The purity of the prepared stabilizers was checked by elemental analyses, melting point, FTIR, NMR and mass spectra. All the results are in good agreement with those previously reported [23] and are shown in Table 1.The prepared maleimido phenyl thiourea stabilizers are efficient antimicrobial agents against *Bacillus subtilis* (*B.subtilis*), *Streptococcus pneumonia* (*S. pneumoniae*) as Gram positive bacteria and *Escherichia coli*(*E. coli*)as Gram negative bacteria and against three crop-threatening pathogenic fungi [*Aspergillus fumigatus (A. fumigatus), Geotricum candidum (G. candidum)*, and *Syncephalastrum racemosum (S. racemosum)*]as indicated from the inhibition zone diameter and minimum inhibitory concentration. The antibacterial activities of these derivatives were more effective against Gram-positive bacteria than Gram-negative bacteria [23].

Table1. *Characterization of the prepared maleimido phenyl thiourea stabilizers*

Stabilizer code	Melting point (^{o}C)	Characteristic IR peaks v (cm^{-1})	Characteristic ^{1}H-NMR signals, δ (ppm)	MS m/z (M^{+})	Elemental analyses[a] %C %H %N %S %Cl
1	205	3463, 3318 (NH), 1649 (C=O), 1707 (C=O, imide), 1600, 1512 (Ph), 829 (maleimide- moiety), 544 (N-C-S)	7.19 (s, 2H, =CH), 7.33-8.058 (m, 9H, ArH), 10.30 (s, 2H, 2NH disappearing on deuteration)	351	61.513.6911.95 9.90 - (61.53) (3.70) (11.96) (9.11) -
2	225	3456, 3365 (NH), 1673 (C=O), 1719 (C=O, imide), 1597, 1542 (Ph), 1395 (CH$_3$), 1075 (C=S), 541 (N-C-S), 824 (maleimide- moiety)	7.17 (s, 2H, =CH), 7.35-8.12 (m, 8H, ArH), 11.55, 12.49 (2s, 2H, 2NH disappearing on deuteration), 2.25 (s, 3H, CH$_3$)	381	60.00 3.9311.078.47 - (59.83) (3.93) (11.03) (8.39) -
3	156	3456, 3275 (NH), 1655 (C=O), 1714 (C=O, imide), 1590, 1511 (Ph), 1051 (C=S), 540 (N-C-S), 830 (maleimide- moiety overlapped with C-Cl)	7.19 (s, 2H, =CH), 7.33- 8.19 (m, 8H, ArH), 10.14, 10.19 (2s, 2H, 2NH disappearing on deuteration)	385	56.053.0910.948.28 9.05 (56.01) (3.11) (10.90) (8.31) (9.09)
4	>300	3466, 3343 (NH, OH), 1686 (C=O), 1711 (C=O, imide &- COOH), 1599, 1509 (Ph), 1064 (C=S), 546 (N-C-S), 833 (maleimide-moiety)	7.19 (s, 2H, =CH), 7.88-8.07 (m, 8H, ArH), 7.51, 7.54 (2s, H, 2NH disappearing on deuteration), 10.6 (s, 1H, 1-COOH)	395	57.883.3410.758.07 - (57.72) (3.29) (10.63) (8.10) -

a Data given between parentheses corresponded to calculated elemental analyses.

2.3. Measurements

FTIR spectra were recorded on a Shimadzu FTIR 8201 PC spectrophotometer (Tokyo, Japan) using KBr pellets.

^{1}H-NMR spectra were recorded with a Jeol 270 MHz spectrophotometer (Tokyo, Japan) in DMSO-d_6 as a solvent and the chemical shifts were recorded in ppm relative to TMS as an internal standard.

Mass spectra were recorded on Shimadzu GCMS-QP 1000 ex spectra Mass spectrometer (Tokyo, Japan) operating at 70 eV.

Elemental analyses were carried out in Perkin-Elmer (Model 2410 series II) C, H, N Analyzer (USA) at the Micro-Analytical center at Cairo University, Giza, Egypt.

Antibacterial activities were investigated using the agar well diffusion method. The activity of tested samples was studied against *B. subtilis* (RCMB 010069) and *S. pneumoniae* (RCMB 010019) as Gram positive bacteria and against *E. coli* (RCMB 010055) as Gram negative bacteria. The activity was determined by measuring the diameter of the inhibition zone (in mm). Each inhibition zone was measured three times by caliper to get an average value. Ampicillin and Gentamicin were used as antibacterial standard drugs [26].

Antifungal activities were investigated by screening the tested samples separately in vitro against *A. fumigatus* (RCMB 02569), *S. racemosum* (RCMB 05925) and *G. candidum* (RCMB 05098) fungi on sabourad dextrose agar plates. The culture of fungi was purified by the single spore isolation technique. The antifungal activity was by agar well diffusion method [27]. The activity was determined by measuring the diameter of the inhibition zone (in mm). Each inhibition zone was performed three times for each fungus. Amphotericin B was used as antifungal standard drug. The minimum inhibition concentration (MIC) of tested samples was determined by counting the colonies using two-fold dilutions of each sample. The MIC was considered to be the lowest concentration that completely inhibits against inoculums comparing with the control, disregarding a single colony or a faint haze caused by the inoculums.

Samples of PVC for thermal degradation were prepared by thoroughly mixing 1g of PVC powder with 0.02 g of the stabilizer in a mortar and 0.2 g of the resulting fine powder was used in each investigation. Mixing of the stabilizers was effected in the range of 0-100 wt% of the maleimido phenyl thiourea stabilizer relative to each of the reference stabilizers. The overall mixed stabilizers concentration was kept constant at 2g/100 g PVC.

Evaluation of the stabilizing efficiency was carried out by measuring the rate of dehydrochlorination using a continuous potentiometric determination of the evolved hydrogen chloride gas at 180°C in air. A detailed description of this method was given elsewhere [28]. The extent of discoloration of the degraded PVC samples was evaluated visually as a function of degradation time.

3. RESULTS AND DISCUSSION

3.1. Effect of Mixed Stabilizers on the Stabilizing Efficiency of Thermally Degraded Rigid PVC

Results of the dehydrochlorination rates of rigid PVC thermally degraded at 180°C, in air, in the presence of mixed stabilizer **2** and each of the three reference stabilizers: DBLC, Cd-Ba-Zn stearate or n-OTM are illustrated in Figs1-3, respectively. The results of Ts values of such combinations are shown in Table 2. Mixing was effected in the range of 0-100 wt% of the stabilizer **2** relative to either of the reference stabilizers used. The overall mixed stabilizers concentration was kept constant at 2 g / 100 g PVC. Results of non-stabilized blank PVC sample and those of the PVC samples stabilized with 2 wt% DBLC, Cd-Ba-Zn stearate, n-OTM reference stabilizers and the organic stabilizer **2** are also given for comparison. The results represent the average of three comparable experiments for each stabilizer or stabilizers mixture.

The results clearly reveal a true synergistic effect resulting from the combination of the stabilizer **2** with any of the reference stabilizers. The synergistic effect is illustrated not only from the improvement in the Ts values of the mixed stabilizers as compared with the values for samples containing only the investigated or the reference stabilizers, but also from the lower rate of dehydrochlorination observed for the mixed stabilizers at latter stages of degradation (i.e. after the thermal stability period). The maximum synergism was achieved when the investigated stabilizer and either of the reference stabilizers were mixed in equivalent weight ratio (i.e. 50%:50%) as shown in Table 2.

Table2. *Effect of mixing maleimido phenyl thiourea 2 with reference stabilizers on the thermal stability period (Ts) of thermally degraded rigid PVC at 180oC in air. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Ts (min)	Weight ratio	Ts (min)	Weight ratio	Ts (min)
2/DBLC		**2**/Cd-Ba-Zn stearate		**2**/n-OTM	
100/0	33	100/0	33	100/0	33
75/25	42	75/25	48	75/25	52
50/50	51	50/50	56	50/50	66
25/75	38	25/75	43	25/75	46
0/100	8	0/100	8	0/100	9

In order to confirm the results obtained in case of mixing the various reference stabilizers with maleimido phenyl thiourea stabilizer **2**, the study of the efficiency of the mixed stabilizers was extended to cover three other maleimido phenyl thiourea stabilizers **1**, **3** and **4.** A similar behavior is also seen when stabilizers **1**, **3** or **4** are mixed with the reference stabilizers (Table3), which gave a strong experimental proof for the results obtained.

Table3. *Effect of mixing maleimido phenyl thiourea stabilizers 1, 3, and 4 with reference stabilizers on the thermal stability period (Ts) of thermally degraded rigid PVC at 180oC in air. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Ts (min)	Weight ratio	Ts (min)	Weight ratio	Ts (min)
1/DBLC		**1**/Cd-Ba-Zn stearate		**1**/n-OTM	
100/0	28	100/0	28	100/0	28
75/25	37	75/25	42	75/25	46
50/50	45	50/50	50	50/50	58
25/75	33	25/75	38	25/75	41
0/100	8	0/100	8	0/100	9
3/DBLC		**3**/Cd-Ba-Zn stearate		**3**/n-OTM	
100/0	25	100/0	25	100/0	25
75/25	33	75/25	38	75/25	42
50/50	41	50/50	45	50/50	53
25/75	31	25/75	34	25/75	37
0/100	8	0/100	8	0/100	9
4/DBLC		**4**/Cd-Ba-Zn stearate		**4**/n-OTM	
100/0	21	100/0	21	100/0	21
75/25	29	75/25	34	75/25	37
50/50	36	50/50	40	50/50	47
25/75	27	25/75	30	25/75	33
0/100	8	0/100	8	0/100	9

In order to find an explanation for the well-defined synergistic action shown when stabilizer **2** is mixed with the reference stabilizers, two experiments were performed. First, heating mixtures of various weight ratios of stabilizer **2** and either the reference stabilizers at 180°C, in air, followed by fractional crystallization, shows no change in the melting point of stabilizer **2** and no detectable loss in its weight fraction, which indicates that there is no chemical reaction between stabilizer **2** and any of the reference stabilizers. The second, comparing the UV spectra of the above mixed stabilizers with those of pure components, shows the absence of any interaction or

complexation between the components of the mixtures as no shift was oberved in the UV bands characteristic of stabilizer **2**. Accordingly, it seems that the synergistic action results from the different mechanisms by which stabilizer **2** and the reference stabilizers work. This fact is experimentally supported by observing the rates of dehydrochlorination in all cases, at various weight ratios of the components of the mixed stabilizers, which are comparable with those characteristic for investigated stabilizer rather than for the reference stabilizers. This indicates that stabilizer **2** and the reference stabilizers act separately through replacement of the labile chlorines and reaction with the liberated hydrogen chloride gas.

These results coincide well with those obtained in case of stabilizers **1**, **3**, and **4** which give an additional proof supporting the different mechanisms by which the investigated and the reference stabilizers work.

On the other hand, the increased stabilizing efficiency of the mixed stabilizer may result from the fact that the phenyl urea moiety of the investigated stabilizers react with the accumulated metal chlorides ($PbCl_2$, $CdCl_2$, $ZnCl_2$ and $SnCl_2$) formed as by-products from reference stabilizers to form complexes with additional stabilizing power [17], and thus the investigated stabilizer, not only removes the deleterious effect of the metal chlorides but also it gives an additional advantage from their transformation into useful new stabilizers.
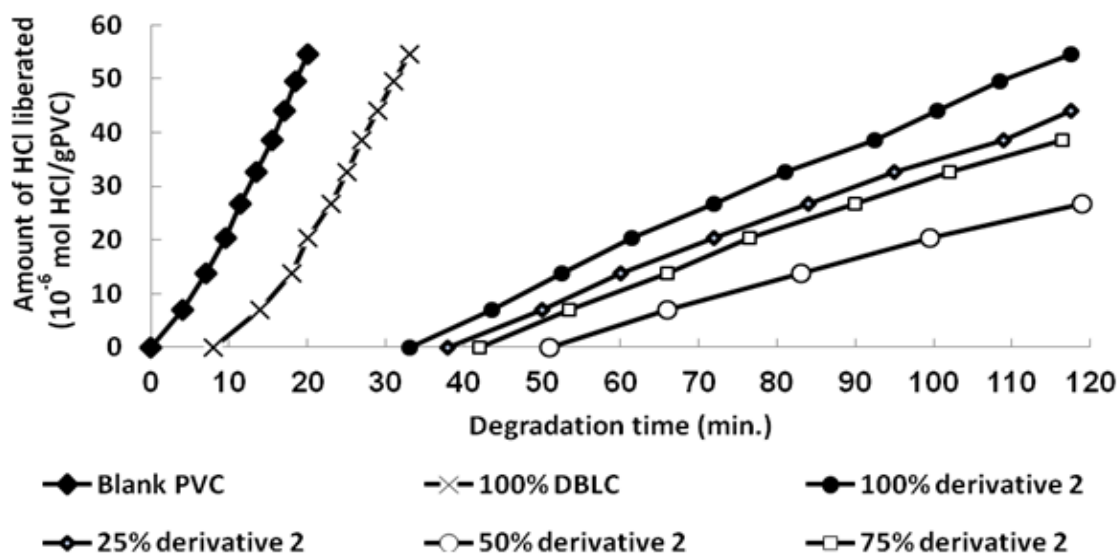
Fig1. *Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180°C, in air. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight: stabilizer **2** and DBLC.*
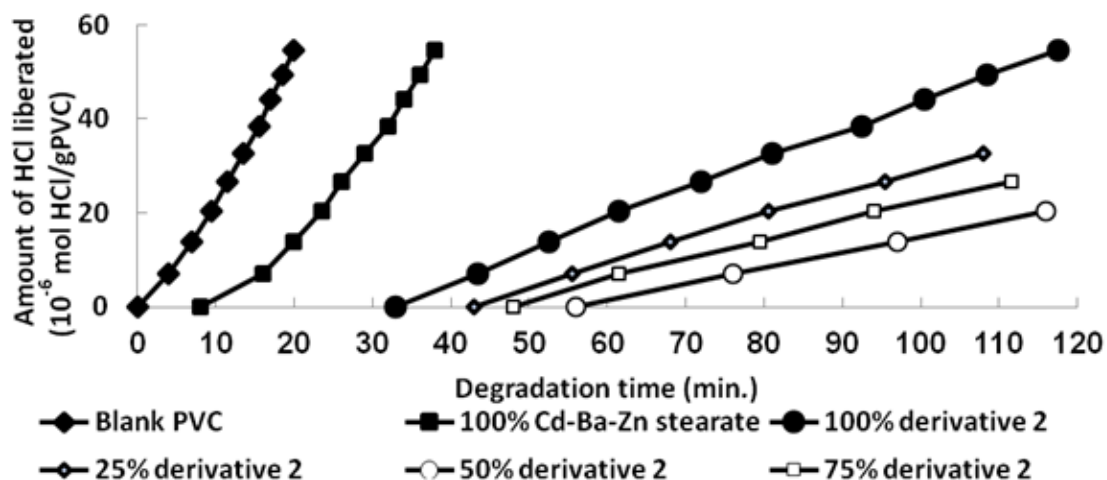
Fig2. *Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180oC, in air. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight: stabilizer 2 and Cd-Ba-Zn stearate.*
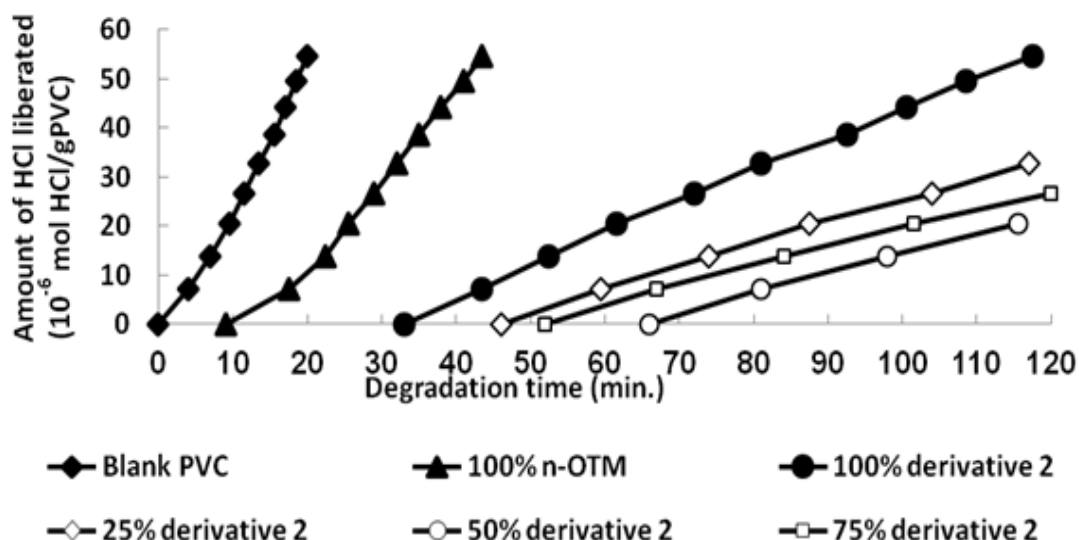
Fig3. *Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180oC, in air. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight: stabilizer 2 and n-OTM.*

3.2. Effect of Mixed Stabilizers on the Extent of Discoloration of Thermally Degraded PVC

The effect of mixing stabilizers **1**, **2**, **3** or **4** with DBLC, Cd-Ba-Zn stearate or n-OTM, in various weight ratios, on the degree of discoloration of thermally degraded rigid PVC is shown in Tables 4-7. All the samples were heated at 180°C, in air, for 60 min. The results clearly reveal that all the mixed stabilizers exhibited a lower extent of discoloration as compared with the reference stabilizer, rather than the investigated stabilizers when they are used separately. In all cases, the samples treated with 1:1 weight ratio of the investigated stabilizer and reference stabilizer showed the least degree of discoloration and consequently the better color stability. These results confirm the synergistic effect between their modes of action.

Table4. *Effect of mixing maleimido phenyl thiourea stabilizer 1 with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180oC, in air, for 60 min. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Color	Weight ratio	Color	Weight ratio	Color
1/DBLC		**1**/Cd-Ba-Zn stearate		**1**/n-OTM	
100/0		100/0		100/0	
75/25		75/25		75/25	
50/50		50/50		50/50	
25/75		25/75		25/75	
0/100		0/100		0/100	

Table5. *Effect of mixing maleimido phenyl thiourea 2 with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180oC, in air, for 60 min. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Color	Weight ratio	Color	Weight ratio	Color
2/DBLC		**2**/Cd-Ba-Zn stearate		**2**/n-OTM	
100/0		100/0		100/0	
75/25		75/25		75/25	
50/50		50/50		50/50	
25/75		25/75		25/75	
0/100		0/100		0/100	

Table6. *Effect of mixing maleimido phenyl thiourea 3 with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180oC, in air, for 60 min. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Color	Weight ratio	Color	Weight ratio	Color
3 /DBLC		**3** /Cd-Ba-Zn stearate		**3** /n-OTM	
100/0		100/0		100/0	
75/25		75/25		75/25	
50/50		50/50		50/50	
25/75		25/75		25/75	
0/100		0/100		0/100	

Table7. *Effect of mixing maleimido phenyl thiourea 4 with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180oC, in air, for 60 min. The overall mixed stabilizers concentration was kept constant at 2 wt % based on PVC weight.*

Weight ratio	Color	Weight ratio	Color	Weight ratio	Color
4/DBLC		**4**/Cd-Ba-Zn stearate		**4**/n-OTM	
100/0		100/0		100/0	
75/25		75/25		75/25	
50/50		50/50		50/50	
25/75		25/75		25/75	
0/100		0/100		0/100	

4. CONCLUSION

Study the effect of mixing the investigated stabilizers together with those used in industry on the efficiency of thermal stabilization of rigid PVC revealed that mixed stabilizers were of great stabilizing efficiency than when they used separately and showed a true synergistic effect. This is illustrated by a remarkable improvement both the Ts values, the rate of dehydrochlorination and the extent of discoloration. The maximum synergism was achieved when the mixed stabilizers are taken in equivalent weight ratio. The observed synergistic effect is most probably attributable to the combination of the mechanisms by which the investigated and the reference stabilizers work. Thus, while the investigated stabilizers work through radical trapping and blocking the radical sites on the polymer chains, the reference ones may either neutralize the hydrogen chloride gas liberated (DBLC) or substitute the labile sites in the polymer chains (Cd-Ba-Zn stearate and n-OTM). Thus, one can conclude that maleimido phenyl thiourea stabilizers, stabilizer **2** in particular, are efficient co-stabilizers for rigid PVC against its thermal degradation.

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