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Material behaviour

Synergistic effect of maleimido phenyl urea derivatives mixed with some commercial stabilizers on the efficiency of thermal stabilization of PVC

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ABSTRACT

Four novel antimicrobial maleimido phenyl urea stabilizers **1**–**4** were synthesized from N-[4-(chlorocarbonyl) phenyl] maleimide with phenyl urea and its derivatives (p-methyl, o-chloro and p-carboxy). The effect of mixing maleimido phenyl urea stabilizer **2** with each of the reference stabilizers, dibasic lead carbonate (DBLC), cadmium-barium-zinc stearate (Cd-Ba-Zn stearate) or n-octyltin mercaptide (n-OTM), on the stabilization efficiency in thermal degradation of rigid PVC at 180 °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 amount of hydrogen chloride gas could be observed, and also from the rate of dehydrochlorination as measured by continuous potentiometric determination, and by the extent of discoloration of the degraded polymer samples. 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 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.

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1. Introduction

Poly(vinyl chloride), PVC, is a material of enormous technical and economic importance. It stands second in the world after polyethylene as regards the production and consumption of a synthetic material. Its extensive autocatalytic dehydrochlorination, with the subsequent formation of conjugated double bonds, on 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 increase in molecular weight as a result of chain scission or cross linking, respectively, which can reduce the useful life of the product [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

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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 for 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 other hand, PVC products for certain applications in the fields of construction, food package, decoration, medicine (e.g. for the fabrication of indwelling catheters in hospital care) and commodities such as construction tubing, films, toys, wallpaper, etc, cannot avoid contamination with microbes during their daily usage. For such applications, a new trend has been established recently 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 urea 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 substitutes that have greater stability (the case of both soap and organotin stabilizer such as cadmium-barium-zinc stearate complex, Cd-Ba-Zn stearate, and n-octyltin mercaptide, n-OTM, respectively). Accordingly, it became of interest to investigate the effect of mixing maleimido phenyl urea stabilizer **2** (which seems to have a relatively higher stabilizing efficiency than other maleimido phenyl urea 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) used in this study was additive free, with a K-value of 70 and supplied by Hüls Co. (Frankfurt, Germany). Cadmium-barium-zinc stearate complex (Cd-Ba-Zn stearate) obtained from G. Siegle and Co. (Stuttgart, Germany), n-octyltin mercaptide (n-OTM) obtained from America Company for PVC manufacturing (Alexandria, Egypt) and dibasic lead carbonate (DBLC) obtained from the National lead Co. (Darmstadt, Germany) were used in this study. P-Amino benzoic acid obtained from Oxford, p-toluidine obtained from Merck, and o-choloro aniline obtained from Schuchard–München 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 urea and its derivatives

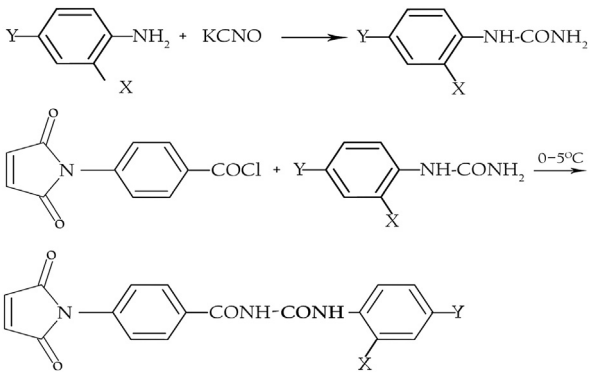
Four maleimido phenyl urea stabilizers **1**–**4** were prepared according to the method described in our previous work [23], as shown in Scheme 1. Briefly, 0.1 mol of potassium cyanate dissolved in 50 ml of warm water was added gradually with continuous stirring to 0.01 mol of the aromatic amine dissolved in 100 ml of 10% acetic acid solution. The reaction mixture was allowed to stand for 30 min, and cooled in ice for another 30 min. The crude (phenyl urea or its derivatives) was filtered, washed with water, recrystallized from boiling water and dried in an oven [25]. 9.42 g (0.04 mol) of N-(4-chloro carbonyl phenyl) maleimide was added gradually to the phenyl urea or its derivatives (0.04 mol) dissolved in least amount of dry cooled acetone, kept stirred for 1 h and poured onto crushed ice to separate the stabilizer which recrystallized from dry benzene.

The purity of the prepared stabilizers was checked by elemental analyses, melting point, IR, 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 urea stabilizers are efficient antimicrobial agents against *B. subtilis* and *S. pneumoniae* as Gram positive bacteria and against *E. coli* as Gram negative bacteria and against *A. fumigatus*, *S. racemosum* and *G. candidum* fungi [23].

2.3. Measurements

FTIR spectra were recorded on a Shimadzu FTIR 8201 PC spectrophotometer using KBr pellets.

^{1}H-NMR spectra were recorded with a JOEL 270 MHz (Tokyo, Japan) spectrophotometer in DMSO-d_6 as a solvent



Scheme 1. Synthesis of maleimido phenyl urea derivatives.

Derivative Code	1	2	3	4
X	H	H	Cl	H
Y	H	CH_3	H	COOH

Table 1
Characterization of the prepared maleimido phenyl urea stabilizers.

Stabilizer code	Melting point (°C)	Characteristic IR peaks ν (cm^{-1})	Characteristic ^{1}H-NMR signals, δ (ppm)	MS m/z	Elemental analyses			
					%C	%H	%N	%Cl
1	151	3471 (NH), 1718 (C=O, amide, imide), 1597, 1507 (Ph), 831 (maleimide- moiety)	7.18 (s, 2H, =CH), 7.47-8.058 (m, 9H, ArH), 7.35 (s, 2H, 2NH disappearing on deuteration)	335 (M^+)	64.41 (64.48)	3.86 (3.88)	12.60 (12.53)	– –
2	183	3468 (NH), 1718 (C=O, amide, imide), 1596, 1507 (Ph), 835 (maleimide- moiety)	7.1 (s, 2H, =CH), 7.47-8.05 (m, 8H, ArH), 7.38 (s, 2H, 2NH disappearing on deuteration), 2.6 (s, 3H, CH_3)	349 (M^+)	65.31 (65.33)	4.00 (4.29)	12.10 (12.03)	– –
3	151	3456, 3366 (NH), 1718 (C=O amide, imide), 1595, 1536 (Ph), 833 (maleimide- moiety)	7.18 (s, 2H, =CH), 7.36- 8.11 (m, 8H, ArH), 6.34 (s, 2H, 2NH disappearing on deuteration)	369 (M^+)	58.53 (58.50)	3.25 (3.30)	11.38 (11.29)	9.48 (9.50)
4	146	3469 (NH), 1725, 1719 (C=O amide, imide &-COOH), 1597, 1507 (Ph), 835 (maleimide- moiety)	7.12 (s, 2H, =CH), 7.47-8.073 (m, 8H, ArH), 7.35 (s, H, 2NH disappearing on deuteration), 10.11 (s, 1H, 1-COOH)	379 (M^+)	60.00 (60.15)	3.44 (3.43)	11.01 (11.08)	– –

and the chemical shifts were recorded in ppm relative to TMS as an internal standard.

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

Elemental analyses were carried out in a 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 with calipers to get an average value. Ampicillin and Gentamicin were used as standard antibacterial 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 the 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 standard antifungal 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 urea 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 continuous potentiometric determination of the evolved hydrogen chloride gas at 180 °C in air. A detailed description of this method has been 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 Figs. 1–3, respectively. The results of Ts values of such

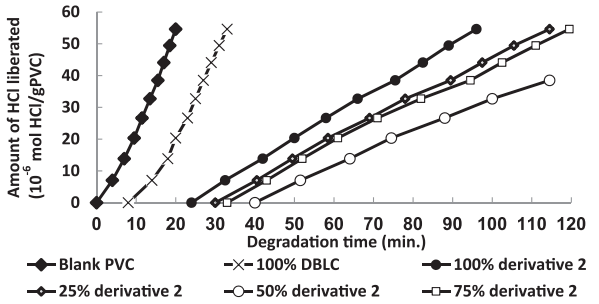


Fig. 1. Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180 °C, in air. The overall mixed stabilizers concentration was kept constant at 2 wt% based on PVC weight: stabilizer **2** and DBLC.

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 stabilizer mixture.

The results clearly reveal a true synergistic effect resulting from the combination of the stabilizer **2** with any

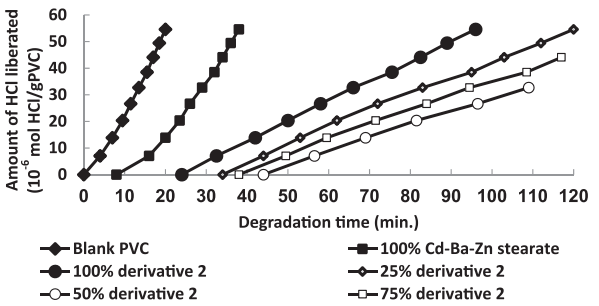


Fig. 2. Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180 °C, in air. The overall mixed stabilizers concentration was kept constant at 2 wt% based on PVC weight: stabilizer **2** and Cd-Ba-Zn stearate.

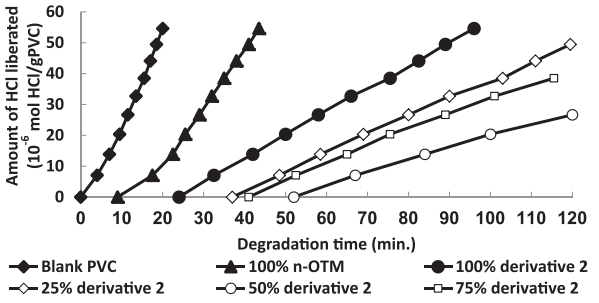


Fig. 3. Effect of mixed stabilizers on the rate of dehydrochlorination of thermally degraded rigid PVC at 180 °C, in air. The overall mixed stabilizers concentration was kept constant at 2 wt% based on PVC weight: stabilizer **2** and n-OTM.

Table 2
Effect of mixing maleimido phenyl urea **2** with reference stabilizers on the thermal stability period (Ts) 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.

Weight ratio	Ts (min)	Weight ratio	Ts (min)	Weight ratio	Ts (min)
2/DBLC		**2**/Cd-Ba-Zn stearate		**2**/n-OTM	
100/0	24	100/0	24	100/0	24
75/25	33	75/25	38	75/25	41
50/50	40	50/50	44	50/50	52
25/75	30	25/75	34	25/75	37
0/100	8	0/100	8	0/100	9

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.

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

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 of the reference stabilizers at 180 °C in air, followed by fractional crystallization, shows no change in

Table 3
Effect of mixing maleimido phenyl urea stabilizers **1**, **3**, and **4** with reference stabilizers on the thermal stability period (Ts) 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.

Weight ratio	Ts (min)	Weight ratio	Ts (min)	Weight ratio	Ts (min)
1/DBLC		**1**/Cd-Ba-Zn stearate		**1**/n-OTM	
100/0	20	100/0	20	100/0	20
75/25	29	75/25	33	75/25	37
50/50	35	50/50	39	50/50	46
25/75	26	25/75	30	25/75	32
0/100	8	0/100	8	0/100	9
3/DBLC		**3**/Cd-Ba-Zn stearate		**3**/n-OTM	
100/0	18	100/0	18	100/0	18
75/25	27	75/25	31	75/25	34
50/50	32	50/50	36	50/50	43
25/75	24	25/75	28	25/75	30
0/100	8	0/100	8	0/100	9
4/DBLC		**4**/Cd-Ba-Zn stearate		**4**/n-OTM	
100/0	15.5	100/0	15.5	100/0	15.5
75/25	24	75/25	27	75/25	30
50/50	29	50/50	32	50/50	38
25/75	22	25/75	24	25/75	27
0/100	8	0/100	8	0/100	9

Table 4
Effect of mixing maleimido phenyl urea stabilizer **1** with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180 °C, 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	

Table 6
Effect of mixing maleimido phenyl urea stabilizer **3** with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180 °C, 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	

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. Secondly, 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 observed 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 of the 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 the 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]. Thus, the investigated stabilizer not only removes the

Table 5
Effect of mixing maleimido phenyl urea stabilizer **2** with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180 °C, 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	

Table 7
Effect of mixing maleimido phenyl urea stabilizer **4** with reference stabilizers on the discoloration of thermally degraded rigid PVC at 180 °C, 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	

deleterious effect of the metal chlorides but also gives an additional advantage from their transformation into useful new stabilizers.

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.

4. Conclusions

Study of 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 are of greater stabilizing efficiency than when they used separately and showed a true synergistic effect. This is illustrated by a remarkable improvement 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 urea stabilizers, stabilizer **2** in particular, are efficient co-stabilizers for rigid PVC against its thermal degradation.

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