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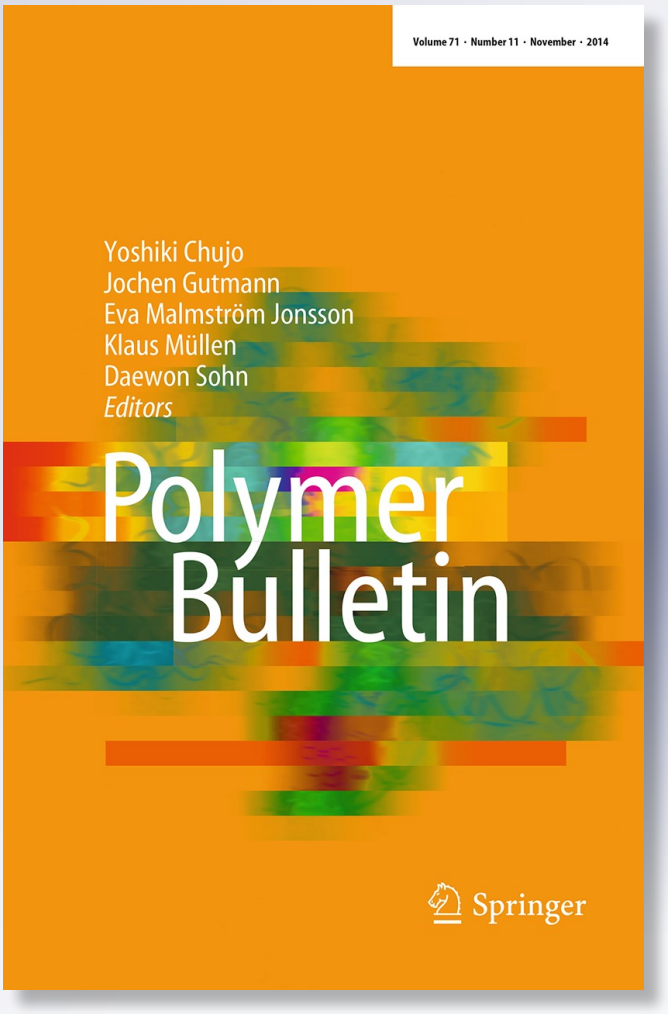

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ORIGINAL PAPER

Thermally stable antimicrobial PVC/maleimido phenyl urea composites

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Abstract Four novel antimicrobial maleimido phenyl urea derivatives were synthesized from *N*-[4-(chlorocarbonyl) phenyl] maleimide with phenyl urea derivatives (*p*-methyl, *o*-chloro and *p*-carboxy). They were characterized by FTIR, ^{1}H-NMR, mass spectra, elemental analyses and antimicrobial activities. These derivatives were investigated as thermal stabilizers for rigid poly(vinyl chloride) at 180 °C in air by measuring the rate of dehydrochlorination and the extent of discoloration. The results reveal the greater stabilizing efficiency of the investigated derivatives as shown by their longer thermal stability periods (Ts) and lower dehydrochlorination rates in relation to dibasic lead carbonate, cadmium-barium-zinc stearate and *n*-octyltin mercaptide industrial stabilizers. The stabilizing efficiency increases with the introduction of electron donating substituent groups in the aromatic ring of the stabilizer molecules. Moreover, the investigated stabilizers impart better color stability for the degraded samples as compared with the reference stabilizers.

Keywords Maleimido phenyl urea derivatives · Antimicrobial activity · PVC · Dehydrochlorination rate · Discoloration degree

N. A. Mohamed (✉) · N. A. Abd El-Ghany · M. M. Fahmy · M. H. Ahmed
Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt
e-mail: namadm@hotmail.com

N. A. Abd El-Ghany
e-mail: dr_nahed_055@yahoo.com

M. M. Fahmy
e-mail: m.fahmy17@yahoo.com

M. H. Ahmed
e-mail: marwa.hosny@resala.org

Introduction

Poly(vinyl chloride) (PVC), has been widely used in the fields of construction materials, food package, decoration, medication (e.g., for the fabrication of indwelling catheters in the hospital care) and commodities such as construction tubing, films, toys, wallpaper, etc. These materials and products cannot avoid smirching with bacteria or microbes during their daily usage so that it is important to develop antibacterial PVC composites for such applications. Some attempts have been performed to prepare antibacterial PVC composites using different antibacterial nanoparticles. Zirconium phosphate containing nano-sized silver particles [1] and TiO_2/Ag^+ nanoparticles [2] were used for these studies. Further, isothiocyanate nucleophilically substituted PVC could also be used as antibacterial PVC [3].

On the other hand, PVC is known to undergo extensive degradation, especially during its molding and applications at high temperatures. Its thermal degradation occurs by autocatalytic dehydrochlorination reaction with subsequent formation of conjugated double bonds [4]. This results in an unacceptable discoloration of the polymer and a loss of its physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain-scission or cross-linking of the polymer molecules, respectively [5–7]. 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 steric order of the monomer units (tacticity) [8–13]. Various kinds of stabilizers have been used to inhibit the thermal degradation of PVC either by reacting with the evolved hydrogen chloride gas, produced as a result of the degradation process, such as basic salts [14], or by displacing the labile chlorine in PVC chains by more stable ester or mercaptide groups such as metallic soaps [15], and esters or mercaptides of dialkyltin [16]. Most of the mentioned stabilizers lead to the formation of heavy metal chlorides as by-products which will act as strong catalysts for the subsequent dehydrochlorination of PVC and may present a serious environmental problem [17, 18]. Various organic ligands have been proposed as co-stabilizers so as to react with these metal chlorides and provide more protection to the polymer [19, 20]. Recently, metal-free and environmentally acceptable fully organic stabilizers have been established for the thermal stabilization of PVC [21–23]. Since the time of fabrication of PVC is relatively short, and determination of the amount of stabilizer consumed after various processing times indicates that most of the stabilizer remains unreacted, the final product contains large amount of heat stabilizer. For this, a new trend has been established based on the use of thermal stabilizers of antimicrobial nature to obtain thermally stable antimicrobial PVC composites [22, 23].

Phenyl urea derivatives represent a class of compounds possessing a wide range of biological activities [24–30]. Important biological properties concerning bactericidal, fungicidal and anticancer properties were also reported for N-substituted maleimides [31–36]. It is known that maleimides are inhibitors of cysteine proteinase or other protein with an essential cysteine. Maleimides interact preferably with the hydrophobic domains of enzymes through the inactivation of sulfhydryl groups. They are usually considered as non-specific toxic and

inexpensive family of products and could be interesting candidates for formation of new antimicrobial activity [37]. N-Substituted maleimides [38] and phenyl urea derivatives [39] have been proven to be effective stabilizers for PVC against thermal degradation. While, the maleimides act as powerful radical traps and can exchange the labile chlorine in the PVC chains for a more stable maleimide moiety; the phenyl urea derivatives act mainly as hydrogen chloride gas absorbers, in addition to their ability to form metal complexes. This property enables them to react with various metal chlorides, which result as by-products from the soap or basic salt stabilizers, thus preventing or at least minimizing their catalytic degradation effect.

In view of the above, it would be expected that maleimido phenyl urea derivatives combine the characteristics of both the maleimides and the phenyl urea, could greatly improve the thermal stability of PVC and could inhibit effectively growth of bacteria and fungi. In the present study, we hereby report the synthesis, characterization and evaluation of antibacterial and antifungal activities of some new maleimido phenyl urea derivatives containing substituent groups at their aromatic rings of phenyl urea parts. It is of our great interest to investigate these derivatives as a new type of antimicrobial agents for stabilization of rigid PVC against thermal degradation and to obtain thermally stable antimicrobial PVC composites. The effect of the substituent group on the inhibition of the thermal degradation of rigid PVC is also investigated.

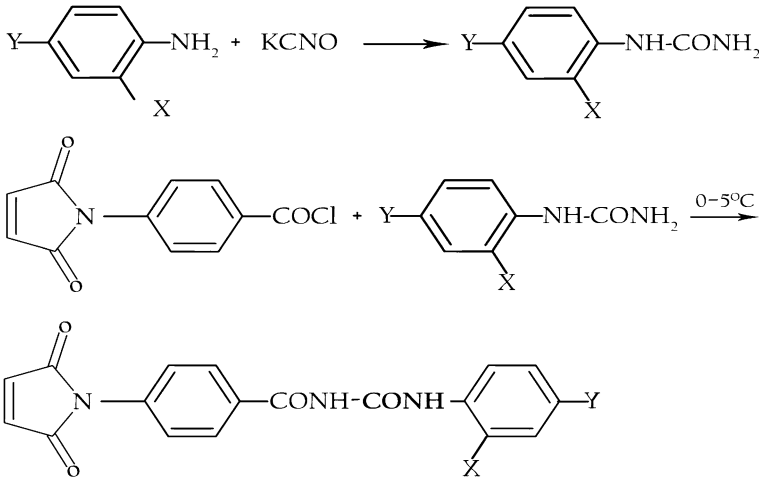
Results and discussion

Synthesis and characterization of the stabilizers

Four maleimido phenyl urea derivatives **1**–**4** (Scheme 1), were synthesized via a low-temperature (0–5 °C) solution (in dry acetone) condensation reaction between *N*-[(4-chloro carbonyl) phenyl] maleimide and either of phenyl urea, *p*-methyl phenyl urea, *o*-chloro phenyl urea or *p*-carboxy phenyl urea. The condensation reaction proceeded through the addition of the solid acid chloride into the cold acetone solution of the phenyl urea derivatives with continuous stirring for 1 h, and then the resulting reaction mixtures were poured on crushed ice to separate the stabilizers.

Derivative code	**1**	**2**	**3**	**4**
X	H	H	Cl	H
Y	H	CH_3	H	COOH

All the derivatives are novel and were obtained in a quantitative yield. The structures of the synthesized derivatives **1**–**4** were ascertained on the basis of their



Scheme 1 Synthesis of maleimido phenyl urea derivatives

consistent FTIR (Fig. 1), ^{1}H-NMR (Fig. 2), mass spectral characteristics and elemental analyses.

Analytical data of derivative **1**

M.p. (°C) 151; Yield-98 %; ^{1}H-NMR (270 MHz, DMSO-d_6) δ (ppm): 7.18 (s, 2H, =CH), 7.47–8.058 (m, 9H, ArH), 7.35 (s, 2H, 2NH disappearing on deuteration); FTIR (KBr pellets) *v* cm^{-1}: 3,471 (NH), 1,718 (C=O, amide, imide), 1,597, 1,507 (Ph), 831 (maleimide-moiety); MS *m/z*: 335 (M^+); Anal. Calcd for $C_{18}H_{13}N_3O_4$: C, 64.48; H, 3.88; N, 12.53. Found: C, 64.41; H, 3.86; N, 12.60.

Analytical data of derivative **2**

M.p. (°C) 183; Yield-96 %; ^{1}H-NMR (270 MHz, DMSO-d_6) δ (ppm): 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); FTIR (KBr pellets) *v* cm^{-1}: 3,468 (NH), 1718 (C=O, amide, imide), 1,596, 1,507 (Ph), 835 (maleimide-moiety); MS *m/z*: 349 (M^+); Anal. Calcd for $C_{19}H_{16}N_3O_4$: C, 65.33; H, 4.29; N, 12.03. Found: C, 65.31; H, 4.0; N, 12.1.

Analytical data of derivative **3**

M.p. (°C) 151; Yield-95 %; ^{1}H-NMR (270 MHz, DMSO-d_6) δ (ppm): 7.18 (s, 2H, =CH), 7.36–8.11 (m, 8H, ArH), 6.34 (s, 2H, 2NH disappearing on deuteration); FTIR (KBr pellets) *v* cm^{-1}: 3,456, 3,366 (NH), 1,718 (C=O amide, imide), 1,595, 1,536 (Ph), 833 (maleimide-moiety); MS *m/z*: 369 (M^+); Anal. Calcd for $C_{18}H_{12}N_3O_4$ Cl: C, 58.53; H, 3.25; N, 11.38; Cl, 9.48, Found: C, 58.5; H, 3.3; N, 11.29; Cl, 9.50.

Analytical data of derivative **4**

M.p. (°C) 146; Yield-95 %; ^{1}H-NMR (270 MHz, DMSO-d_6) δ (ppm): 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); FTIR (KBr pellets) *v* cm^{-1}: 3469 (NH), 1725, 1719 (C=O

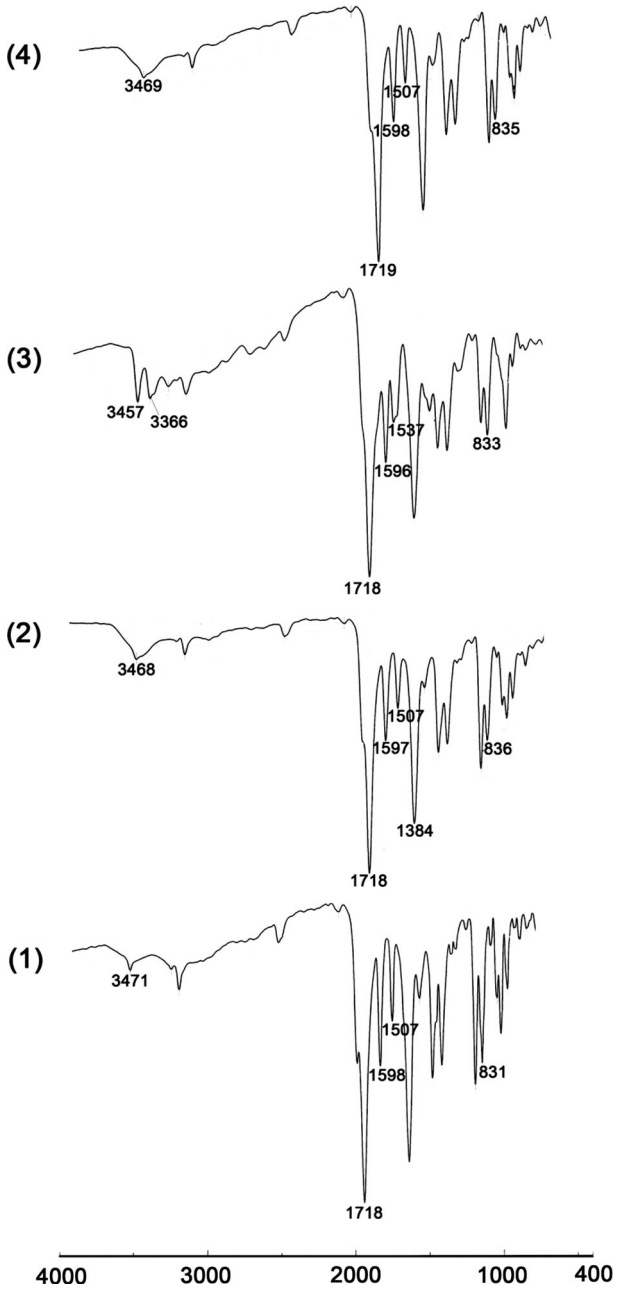


Fig. 1 FTIR spectra of maleimido phenyl urea derivatives

amide, imide &–COOH), 1,597, 1,507 (Ph), 835 (maleimide-moiety); MS *m/z*: 379 (M^+); Anal. Calcd for $C_{19}H_{13}N_3O_6$: C, 60.15; H, 3.43; N, 11.08. Found: C, 60; H, 3.44; N, 11.01.

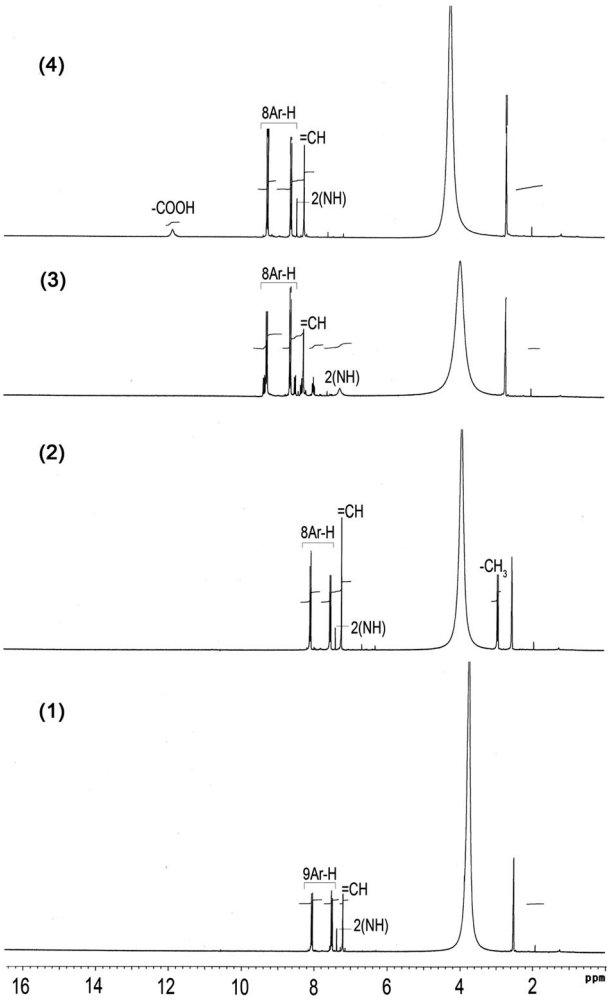


Fig. 2 [1]H-NMR spectra of maleimido phenyl urea derivatives

Antimicrobial activity of maleimido phenyl urea derivatives

Four maleimido phenyl urea derivatives **1**–**4** were screened in vitro for their antimicrobial activities against two Gram-positive bacteria *S. pneumoniae and B. subtilis* and Gram-negative bacteria *E. coli* and three fungal strains *A. fumigates, S. racemosum and G. candidum* by agar diffusion method using *Ampicillin*, *Gentamicin* and *Amphotericin* B as control drugs for antibacterial and antifungal activities, respectively. The results of antimicrobial evaluation are presented in Tables 1, 2, 3, and 4. These compounds showed higher antimicrobial activity and in some cases reached to that of the standard used drugs.

Table 1 Inhibition indices of maleimido phenyl urea derivatives against *B. subtilis, S. pneumoniae* and *E. coli*

Samples	Inhibition zone (mm)		
	Tested bacteria		
	B. subtilis (RCMB 010069)	*S. pneumoniae* (RCMB 010019)	*E. coli* (RCMB 010055)
1	20.9 ± 0.44	18.8 ± 025	18.9 ± 0.58
2	16.4 ± 0.19	15.1 ± 0.58	11.6 ± 0.19
3	22.3 ± 0.44	19.8 ± 0.44	19.1 ± 0.18
4	26.4 ± 0.58	21.4 ± 0.37	20.7 ± 0.18
Ampicillin	29.8 ± 0.15	21.6 ± 0.21	–
Gentamicin	–	–	22.8 ± 0.22

Table 2 MIC values of some selective maleimido phenyl urea derivatives against *B. subtilis, S. pneumoniae* and *E. coli*

Samples	Minimum inhibitory concentration (MIC) (μg/ml) Tested bacteria		
	B. subtilis (RCMB 010069)	*S. pneumoniae* (RCMB 010019)	*E. coli* (RCMB 010055)
4	0.12	1.95	3.9
2	0.98	3.9	7.8
Ampicillin	0.015	0.98	–
Gentamicin	–	–	0.98

Table 3 Inhibition indices of maleimido phenyl urea derivatives against *G. candidum*, *A. fumigatus* and *S. racemosum*

Samples	Inhibition zone (mm)		
	Tested fungi		
	G. candidum (RCMB 05098)	*A. fumigatus* (RCMB 02569)	*S. racemosum* (RCMB 05925)
1	20.4 ± 0.37	17.2 ± 058	19.3 ± 0.44
2	16.4 ± 0.37	13.3 ± 0.19	11.5 ± 0.25
3	21.3 ± 0.58	19.6 ± 0.25	20.2 ± 0.25
4	26.7 ± 0.19	23.4 ± 0.44	21.5 ± 0.58
Amphotericin B	22.8 ± 0.11	20.3 ± 0.19	26.7 ± 0.11

The antibacterial activity of the stabilizers

The results showed that maleimido phenyl urea derivatives **1**–**4** are effective in inhibiting the growth of the bacteria as indicated from the inhibition zone diameter ranging from 11.6 ± 0.19 to 26.4 ± 0.58 mm against tested bacteria (Table 1). Among these four derivatives, compounds **3**, **4** showed the highest antibacterial

Table 4 MIC values of some selective maleimido phenyl urea derivatives against *G. candidum, A. fumigatus* and *S. racemosum*

Samples	Minimum inhibitory concentration (MIC) (μg/ml)		
	Tested fungi		
	G. candidum (RCMB 05098)	*A. fumigatus* (RCMB 02569)	*S. racemosum* (RCMB 05925)
4	0.12	0.49	0.98
2	1.95	7.81	3.9
Amphotericin B	0.12	0.98	1.95

activities. This may be due to the presence of withdrawing substituent on the benzene ring (–Cl and –COOH) while compound **2** exhibited the lowest antibacterial activity which may be attributed to the presence of electron releasing group ($-CH_3$). These results were supported by the higher inhibition zone diameter (Table 1) and the lower MIC values (Table 2) of compound **4** against tested bacteria; the role of electron withdrawing group in improving antibacterial activity is supported by the studies of Sharma et al. [40].

Moreover, it was found that the antibacterial activities of these derivatives were more effective against Gram-positive bacteria than Gram-negative bacteria (Table 1). As the strongest derivative **4** caused inhibition zone diameter for *B. subtilis* and *S. pneumoniae* of 26.4 ± 0.58 and 21.4 ± 0.37 mm, respectively, corresponded to 20.7 ± 0.18 mm for *E. coli*. This may be attributed to their different cell wall. The cell wall of Gram-positive bacteria is fully composed of peptide polyglycogen. The peptidoglycan layer is composed of networks with plenty of pores, which allow foreign molecules to come into the cell without difficulty and allow more rapid absorption of ions into the cell. But the cell wall of the Gram-negative bacteria is made up of a thin membrane of peptide polyglycogen and an outer membrane constituted of lipopolysaccharide, lipoprotein and phospholipids. Because of the complicated bilayer cell structure, the outer membrane is a potential barrier against foreign molecules [41]. Therefore, these derivatives have different effects on the two kinds of bacteria. An additional evidence for the greater activity of these derivatives against Gram-positive bacteria than that against Gram-negative bacteria comes from their minimum inhibitory concentration, since the minimum inhibitory concentration values of the derivative **4** against *B. subtilis* and against *S. pneumoniae* were 0.12 and 1.95 μg/ml, respectively; the minimum inhibitory concentration value against *E. coli* was 3.9 μg/ml. Further, the deduced pattern of the antibacterial activity of the synthesized compounds on the tested bacteria is in the following order: *B. subtilis* > *S. pneumoniae* > *E. coli*

The antifungal activity of the stabilizers

The results showed that maleimido phenyl urea derivatives **1**–**4** are effective in inhibiting the growth of the fungi as indicated from their inhibition zone diameter

which ranging from 11.5 ± 0.25 to 26.7 ± 0.19 (Table 3). Their efficiency may be attributed to the ability of their molecules to diffuse inside the hyphae interfering on the enzymes activity responsible for the fungus growth which may lead to a disturbance of the enzyme activities responsible for the growth criteria, instead of the adsorption of the insoluble compounds on the fungal hyphae surface, it was found from the results that derivatives **3**, **4** are of higher antifungal activities than derivatives **1**, **2**. This may be due to its higher hydrophilicity which allows them to introduce easily inside the hyphae of the fungi and thus enhance the diffusion of the active ingredient inside the pathogens and inhibit their growth. Moreover, as shown in Tables 3 and 4, derivative **4** of the highest antifungal activity exhibits higher inhibition zone diameter (26.7 ± 0.19, 23.4 ± 0.44 and 21.5 ± 0.58 mm) and lower MIC values (0.12, 0.49 and 0.98 μg/ml) against tested fungi corresponding to inhibition zone diameter (22.8 ± 0.11, 20.3 ± 0.19 and 26.7 ± 0.11 mm) and MIC values (0.12, 0.98 and 1.95 μg/ml) for reference standard *Amphotericin* B.

Stabilization of thermally degraded rigid PVC using various maleimido phenyl urea derivatives

Results of the dehydrochlorination of rigid PVC stabilized by various maleimido phenyl urea derivatives and thermally degraded at 180 °C, in air, are shown in Fig. 3. Data of the non-stabilized blank PVC and those of the samples stabilized by DBLC, n-OTM and Cd-Ba-Zn stearates reference stabilizers are also given for comparison. All the stabilizers were used in a concentration of 2 wt% based on PVC weight and the results represent the average of three comparable experiments of each stabilizer. The results clearly reveal the greater stabilizing efficiency of these compounds relative to that of the reference stabilizers. This is indicated not only by

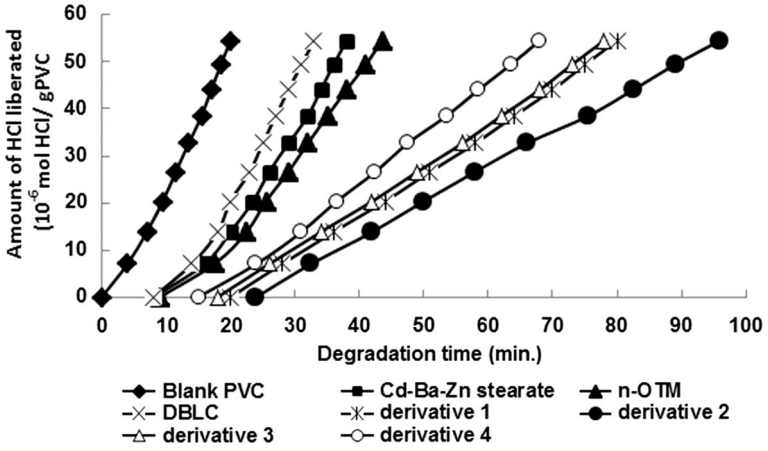


Fig. 3 Rate of dehydrochlorination of rigid PVC at 180 °C, in air, in presence of various maleimido phenyl urea derivatives and reference stabilizers. All the stabilizers were used in a concentration of 2 wt% based on PVC weight

Table 5 Thermal stability (Ts) of rigid PVC thermally degraded at 180 °C, in air, in the presence of the maleimido phenyl urea stabilizers and reference stabilizers. All the stabilizers were used in concentration of 2 wt% based on PVC weight

Stabilizer code	Ts (min)	Stabilizer code	Ts (min)
Blank PVC	0	**1**	20
DBLC	8	**2**	24
Cd-Ba-Zn stearate	8	**3**	18
n-OTM	9	**4**	15

the longer thermal stability periods (Ts) during which no detectable amounts of hydrogen chloride are liberated (Table 5), but also by the lower rates of dehydrochlorination during the subsequent stages of degradation (Fig. 3). The thermal stability period of compound **2** is almost three times higher than the values obtained for the reference stabilizers.

It has been previously suggested that maleimides owe their stabilizing efficiency to the replacement of the labile chlorine atoms on PVC chains by a relatively more thermally stable stabilizer moiety [38]. The stabilizers' efficiency is attributed to their potencies to intervene with the PVC radical degradation process. This most probably occurs not only through trapping the radical species in the degradation process, but also by blocking the radical sites created on PVC chains. The radical attack seems to occur first on the ethylenic carbon–carbon double bond, followed by cleavage of the imide linkages during the later stages of degradation. This mode of action has previously been published, together with experiments to prove it [38]. Furthermore, phenyl urea derivatives are efficient thermal stabilizers for rigid PVC. They exhibit their stabilizing efficiency through effective absorption of the degradation products (HCl gas) by their basic groups [39]. In view of structural similarity of the investigated stabilizers to maleimide combined with phenyl urea, their mechanism is outlined by assuming that their first part (maleimide) can work as radical trapper, while, their other part (phenyl urea) acts as HCl absorber. The data also demonstrate how the Ts and the rate of dehydrochlorination are affected by the type of the substituent group in the aromatic ring of the phenyl urea part (–CH_3, –Cl and –COOH groups) of the stabilizers. This indicates the important role played by the substituent groups in the aromatic ring in the stabilization process. The introduction of the –CH_3 group into the phenyl ring leads to an appreciable improvement in both Ts and the rate of dehydrochlorination. This may be attributed to the nature of this substituent (electron releasing substituent), which can donate electrons toward both the phenyl urea and ethylenic carbon–carbon double bond, resulting in higher stabilizing efficiency relative to that of non-substituted derivative **1**. On the other hand, derivatives **3** and **4** exhibited lower Ts and higher rate of dehydrochlorination than derivative **1**. This can be explained due to the presence of electron withdrawing groups –Cl and –COOH which can withdraw electrons away from the phenyl urea group and ethylenic carbon–carbon double bond leading to a decrease in their stabilizing effect on PVC chains to some extent. Furthermore, the stabilizing effect of derivative **3** was greater than derivative **4**; this is due to the greater accepting power of –COOH group relative to that of the –Cl group.

Effect of the stabilizer concentration on the stabilization efficiency of the thermally degraded rigid PVC

It was useful to identify the least amount of investigated stabilizers that can achieve better stabilizing efficiency compared with the reference stabilizers; so, the study was extended to determine the lowest amount of the investigated stabilizers which can provide stabilizing power comparable with the reference stabilizers. Results of the Ts periods and the rates of dehydrochlorination of PVC stabilized with the investigated stabilizers in different concentration (0.5, 1 and 2 wt% based on PVC weight), are compared with those of the three reference stabilizers taken in 2 wt% (Fig. 4; Table 6).

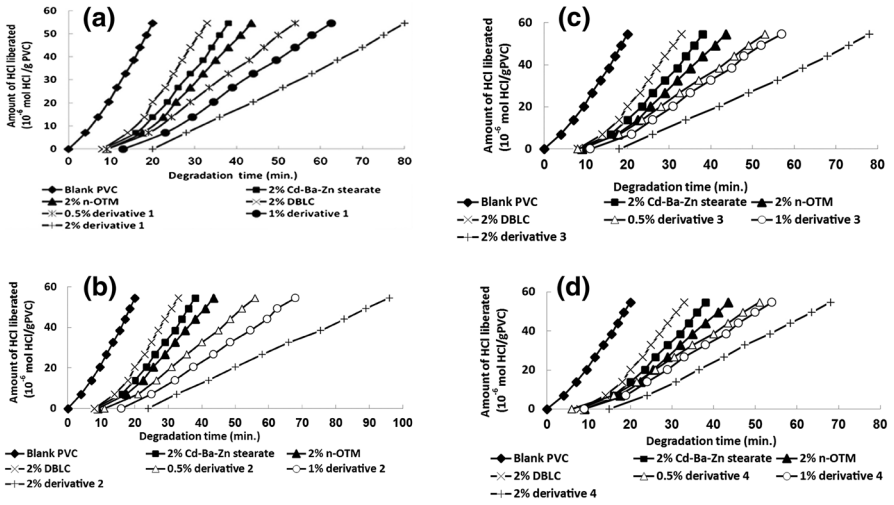


Fig. 4 Effect of the maleimido phenyl urea derivatives concentration on the rate of dehydrochlorination of thermally degraded rigid PVC at 180 °C, in air: **a** derivative *1*, **b** derivative *2*, **c** derivative *3*, **d** derivative *4*

Table 6 Effect of the maleimido phenyl urea stabilizers concentration on the thermal stability period (Ts) of rigid PVC thermally degraded at 180 °C, in air

Stabilizer code	Ts (min), stabilizer concentration (wt% of PVC)		
	0.5	1	2
1	9	13	20
2	11	16	24
3	8	11	18
4	6	9	15
DBLC	–	–	8
Cd-Ba-Zn stearate	–	–	8
n-OTM	–	–	9

The results show the greater efficiency of the investigated stabilizers even at lower concentration (0.5–1.0 wt% based on PVC weight) relative to those of the reference stabilizers (2 wt% based on PVC weight). This was illustrated not only from the higher Ts values (Table 6), but also from the lower rates of dehydrochlorination at subsequent stages of degradation (Fig. 4). The greater efficiency of the investigated stabilizers is most probably not only due to their possession of various centers of reactivity that can act as traps for radical species resulting during the degradation process, but also due to the ability to react with the evolved HCl gas.

Effect of the stabilizers on the discoloration of thermally degraded rigid PVC

It was found that maleimido phenyl urea stabilizers lowered the extent of discoloration of PVC samples relative to blank PVC and PVC stabilized with any of the reference stabilizers as shown in Table 7. This reflects the greater stabilizing efficiency of the investigated stabilizers through the displacement of the labile chlorine atoms by more thermally stable stabilizer moiety which disrupts the formation of conjugated double bonds that are responsible for discoloration. Moreover, the lowering of the extent of discoloration in presence of the investigated stabilizers is most probably due to their dienophilic property which allows them to intervene with the conjugated double bonds formed on the PVC chains at subsequent stages of degradation process by Diels–Alder type of addition. The good color of the dibutylin maleate stabilizer has been attributed to the same type of addition reaction [42].

Experimental section

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 [43].

Preparation of maleimido phenyl urea and its derivatives

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

Table 7 Extent of discoloration of thermally degraded rigid PVC at 180 °C, in air, for various time intervals in the presence of different stabilizers. All the stabilizers were used in concentration of 2 wt% based on PVC weight

Stabilizer code	Color at 0 min	Color at 20 min	Color at 40 min	Color at 60 min
Blank PVC				
DBLC				
Cd-Ba-Zn stearate				
n-OTM				
1				
2				
3				
4				

dried in oven [44]. 9.42 g (0.04 mol) of *N*-(4-chloro carbonyl phenyl) maleimide was added portion-wise to the phenyl urea or its derivatives (0.04 mol) dissolved in THE least amount of dry cooled acetone, kept stirring for 1 h, and poured on crushed ice to separate the stabilizer which recrystallized from dry benzene.

Measurements

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

- ^{1}H-NMR spectra were recorded with a Jeol 270 MHz (Tokyo, Japan) spectrophotometer 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 GCMS-QP 1000 ex spectra Mass spectrometer (Shimadzu, 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 [45].

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 [46]. 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 1 g of PVC powder with 2 wt% of the stabilizer in a mortar and 0.2 g of the resulting fine powder was used in the investigation. 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 [47]. The extent of discoloration of the degraded PVC samples was evaluated visually as a function of degradation time.

Conclusions

The prepared maleimido phenyl urea derivatives 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. They are also efficient stabilizers for rigid PVC against thermal degradation even if they are used in lower concentrations compared with industrial stabilizers

such as DBLC, Cd-Ba-Zn stearate and n-OTM. The investigated stabilizers lower the degree of discoloration of the degraded PVC samples. From the above, it is possible to recommend the use of maleimido phenyl urea derivatives as antimicrobial thermal stabilizers for rigid PVC, to obtain thermally stable antimicrobial PVC/maleimido phenyl urea composites.

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