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Thermogravimetric analysis in the evaluation of the inhibition of degradation of rigid poly(vinyl chloride) using biologically active phthalimido aromatic hydrazide derivatives

Nadia A. Mohamed*, Nahed A. Abd El-Ghany, Mona M. Fahmy

Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt

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ABSTRACT

Four novel antimicrobial phthalimido aromatic hydrazide derivatives were synthesized from N-(4-chlorocarbonylphenyl) phthalimide with benzhydrazide, salicylhydrazide, *p*-aminobenzohydrazide or *p*-aminosalicylhydrazide. They were characterized by FTIR, ^{1}H NMR, mass spectra, elemental analyses and antimicrobial activities. These derivatives were investigated as thermal stabilizers for rigid PVC using thermogravimetric analysis technique, in nitrogen. The results revealed the greater stabilizing efficiency of the investigated derivatives as shown by their higher initial decomposition temperature and higher residual weight percent in relation to dibasic lead carbonate (DBLC), cadmium-barium-zinc (Cd–Ba–Zn) stearate and n-octyltin mercaptide (n-OTM) industrial stabilizers. The stabilizing efficiency increased with the introduction of electron donating substituent groups in the aromatic ring of the phthalimido aromatic hydrazide derivatives.

1. Introduction

Poly (vinyl chloride), PVC, has been widely used in the fields of construction materials, 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. 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]. 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) [6]. 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 degradation process, such as basic salts, or by displacing the labile chlorine in PVC chains by more stable ester or mercaptide groups, such as metallic soaps, and esters or mercaptides of dialkyltin [7]. Most of the mentioned stabilizers lead to the formation of heavy metal chlorides as byproducts which will act as strong catalysts for the subsequent dehydrochlorination of PVC and may present a serious environmental problem [8]. Various organic ligands have been proposed as co-stabilizers so as to react with these metal chlorides and provide more protection to the polymer [9]. Recently, metal-free and environmentally acceptable fully organic stabilizers have been established for the thermal stabilization of PVC [10–12]. Because 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

* Corresponding author.
E-mail address: namadm@hotmail.com (N.A. Mohamed).

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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 [11,12].

N-Substituted phthalimides constitute an interesting class of organic compounds having a wide range of applications in many fields such as medicine, pharmacology, biology, chemistry and physics. They have a great deal of attention due to their biological activity such as antibacterial [13–15], antifungal [14], anti-inflammatory [16–18], and antitumor [19–22]. The hydrazide-hydrazone derivatives represent a class of compounds possessing a wide range of biological activities such as antimicrobial [23], antimycobacterial [24], antitumor [25], anti-inflammatory [26], trypanocidal [27], antimalarial [28], and anti-human immunodeficiency virus activities [29].

N-Substituted phthalimides [30] and aromatic hydrazides [31] have been proven to be effective stabilizers for PVC against thermal degradation. The stabilizing efficiency of the N-substituted phthalimides are strongly affected both by the nature and position of the substituents in the aryl ring being greater for substituents of the electron donating nature and lower for those having electron withdrawing effect; while the non-substituted derivative being in the middle [30]. Further, polymers bearing the phthalimide moieties as pendant groups exhibit relatively high thermal stability [32,33]. On the other hand, the stabilizing efficiency of the aromatic hydrazides increased with increasing the number of the hydrazide linkages as well as with the introduction of electron donating substituents in the phenyl ring of the stabilizer molecule [31].

In view of the above, it would be expected that phthalimido aromatic hydrazide derivatives combine the characteristics of both of the phthalimides and the aromatic hydrazides which could greatly improve the thermal stability of PVC and could inhibit effectively the 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 phthalimido aromatic hydrazides containing substituent groups at their aromatic rings of the hydrazide part. It is of our great interest to investigate these derivatives as new types of antimicrobial agents for the 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.

2. Experimental

2.1. Materials

Commercial PVC (suspension) used in this study had a K-value of 70 and was supplied by Hüls Co. (Frankfurt, Germany). Cadmium-barium-zinc (Cd–Ba–Zn) stearate complex was obtained from G. Siegle and Co. (Stuttgart, Germany), di-n-octyltin bis (isooctylmercaptoacetate) (n-octyltin mercaptide, n-OTM) was supplied by Nitto Kasei Co., Ltd. (Osaka, Japan), dibasic lead carbonate (DBLC) was obtained from the National lead Co. (Darmstadt, Germany) and *p*-aminobenzhydrazide was obtained from Nacalai Tesque (Kyoto, Japan) were also used in this study. N-(4-chlorocarbonyl phenyl) phthalimide was synthesized following the method described by Oishi and Fujimoto [34]. Benzhydrazide, salicylhydrazide, and *p*-aminosalicylhydrazide were prepared from the corresponding acids by two-step procedure in which the acid was esterified to its methyl ester followed by reaction of the produced ester with hydrazine hydrate [35].

2.2. Preparation of the phthalimido aromatic hydrazide derivatives

Phthalimido aromatic hydrazide derivatives **1**–**4** (see Scheme 1) were synthesized by dissolving 1 mol of benzhydrazide, salicylhydrazide, *p*-aminobenzhydrazide, or *p*-aminosalicylhydrazide in 100 ml of *N,N*-dimethyl formamide (DMF), and allowed to cool at −10 °C using an ice-salt bath for 15 min. Then, 1 mol of solid N-(4-chlorocarbonyl phenyl) phthalimide was added slowly and then stirred during 1 h. The cooling bath was removed and the temperature of condensation reaction was allowed to rise gradually to room temperature and maintained for an additional 2 h with stirring. The reaction mixtures were precipitated in 500 ml of methanol-water mixture (1:2), washed with a solution of sodium carbonate to remove any residual acid, which may be formed as a result of decomposition of the acid chloride, washed repeatedly with distilled water, methanol and finally dried in a vacuum oven at 80 °C overnight. As the reaction rate of the hydrazide group with the acid chloride group is seven times faster than that of the amino group [36], the synthesis of the amino derivatives (**3** and **4**) was based on the selective reactivity of the acid chloride with the hydrazide group of aminobenzhydrazide and aminosalicylhydrazide, respectively. All the derivatives and particularly the derivatives 3 and 4 were extensively purified by repeated precipitation from their DMF solutions using methanol-water mixture (1:2). The elemental analysis and MS m/s (M^+) data of these derivatives agreed well with the theoretical values (Table 1).

2.3. Measurements

The Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR 8201 PC spectrophotometer using KBr pellets.

The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Jeol 270 MHz (Tokyo, Japan) spectrophotometer in dimethyl sulfoxide DMSO-d_6 as a solvent and the chemical shifts were recorded in ppm relative to tetramethyl silane (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.

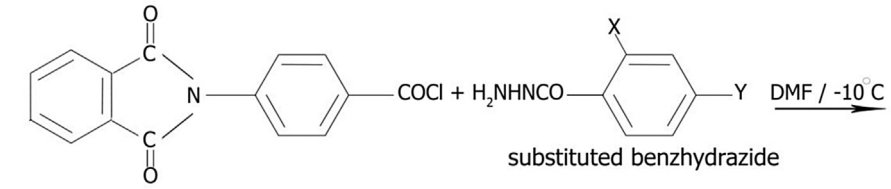
Elemental analyses were carried out in Perkin-Elmer (Model 2410 series II) C, H, N Analyzer (USA) at the Micro-Analytical center at Cairo University, Giza, Egypt.

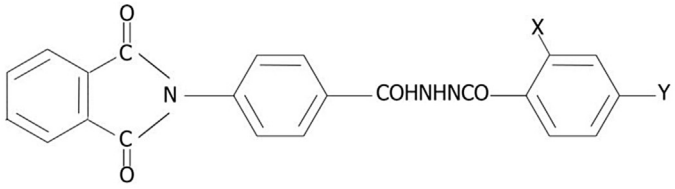
Antibacterial activities of the prepared derivatives against *Bacillis subtilis* (*B. subtilis*, RCMB 010069) and *Streptococcus pneumoniae* (*S. pneumoniae*, RCMB 010019) as Gram-positive bacteria and against *Escherichia coli* (*E. coli*, RCMB 010055) as Gram-negative bacteria were investigated by measuring the diameter of the inhibition zone (in mm) using the agar well diffusion method [37]. Ampicillin and Gentamicin were used as antibacterial standard drugs.

Antifungal activities were investigated by screening the prepared derivatives separately in vitro against *Aspergillus fumigatus* (*A. fumigatus*, RCMB 02569), *Syncephalastrum racemosum* (*S. racemosum*, RCMB 05925) and *Geotricum candidum* (*G. candidum*, RCMB 05098) fungi. The antifungal activities were investigated by measuring the diameter of the inhibition zone (in mm) using the agar well diffusion method [38]. Amphotericin B was used as antifungal standard drug.

The minimum inhibition concentration (MIC) was determined by counting the colonies using two-fold serial dilutions of each derivative. The MIC was considered to be the lowest concentration that completely inhibits against inoculums compared with the control, disregarding a single colony or a faint haze caused by the inoculums.

Thermogravimetric analysis measurements were performed using Shimadzu TGA-50H Thermal Analyzer, under nitrogen (30 ml min^{-1}) from room temperature to 500 °C with a heating rate of 10 °C min^{-1}, where approximately 20 mg of sample was required. The investigated derivatives and blank PVC powder were analyzed





Derivatives code	1	2	3	4
X	H	OH	H	OH
Y	H	H	NH_2	NH_2

Scheme 1. Synthesis of novel phthalimido aromatic hydrazide derivatives.

Table 1
Characterization of the prepared phthalimido aromatic hydrazide stabilizers.

Derivative code	Melting point (°C)	Characteristic FTIR peaks, ν (cm^{-1})	Characteristic ^1H NMR signals, δ (ppm)	MS m/z (M^+)	Elemental analyses[a]			
					%C	%H	%N	%O
1	>300	3462, 3327 (NH), 3063, 3024 (=CH), 1606, 1579 (Ph), 1650(C=O, amide), 1704 (C=O, imide), 848 (phthalimide- moiety)	7.50–8.10 (m, 13H, ArH), 10.5, 10.6 (2s, 2H, 2NH) disappearing on deuteration	385	68.57 (68.53)	3.90 (3.80)	10.91 (10.90)	16.62 (16.77)
2	>300	3456 (OH), 3348–3291 (NH), 3063, 3029 (=CH), 1641 (C=O, amide), 1716 (C=O, imide), 1605, 1492 (Ph), 844 (phthalimide- moiety)	6.9–8.102 (m, 12H, ArH), 10.75, 10.81 (2s, 2H, 2NH disappearing on deuteration), 11.94–11.99 (s, broad, 1H, OH)	401	65.84 (65.80)	3.74 (3.83)	10.47 (10.43)	19.95 (19.94)
3	>300	3459, 3360 (NH), 3150 (=CH), 1605, 1506 (ph), 1655 (C=O, amide), 1712 (C=O, imide), 846 (phthalimide- moiety)	6.58–8.13 (m, 12H, ArH), 10.07–10.64 (2s, 2H, 2NH disappearing on deuteration); 5.75 (s, broad, 2H, NH_2 disappearing on deuteration)	400	66.00 (66.01)	4.00 (3.99)	14.00 (13.90)	16.00 (16.10)
4	>300	3466 (OH), 3367, 3311 (NH), 3083 (=CH), 1605, 1483(ph), 1645(C=O, amide), 1711 (C=O, imide), 847(phthalimide- moiety)	7.58–8.095 (m, 11H, ArH), 5.9, 6.01 (2s, 2H, NH_2 disappearing on deuteration), 11.2, 11.5 (2s, 2H, 2NH disappearing on deuteration), 6.1 (s,1H, OH),	416	63.46 (63.40)	3.85 (3.87)	13.46 (13.97)	19.23 (18.76)

[a] Data given between parentheses corresponded to experimental elemental analyses.

individually followed by stabilized PVC samples prepared by thoroughly mixing in a mortar 1 g of PVC powder with 20 mg of the derivative. From this analysis, the thermograms were obtained illustrating the sample's weight loss or sample's residual weight.

3. Results and discussion

3.1. Synthesis and characterization of the phthalimido aromatic hydrazide derivatives

Four phthalimido aromatic hydrazide derivatives **1**–**4** (Scheme 1) were synthesized via a low temperature (−10 °C) solution (in anhydrous DMF) condensation reaction between N-(4-chlorocarbonylphenyl) phthalimide (1 mol) and benzhydrazide, salicylhydrazide, *p*-aminobenzhydrazide or *p*-aminosalicylhydrazide (1 mol). The condensation reaction proceeded through the addition of the solid acid chloride into the cooling DMF solution of the hydrazide. The resulting condensation reaction mixtures were precipitated into methanol-water mixture, filtered and dried in vacuum at 80 °C overnight. All the derivatives are novel and were obtained in a near-quantitative crude yield which ranged between 98.2 and 99.4%.

The structures of the synthesized derivatives **1**–**4** were ascertained on the basis of their consistent elemental analyses, FTIR, ^1H NMR and mass spectral characteristics (Table 1, Figs. 1 and 2). The functional groups (X, Y) were chosen based on their electron donor potency, being *o*- and *p*-directing, which increased the electron density on the conjugated structure of the phthalimido aromatic hydrazides, and consequently increased their potency to interact with the degradative products of PVC chains.

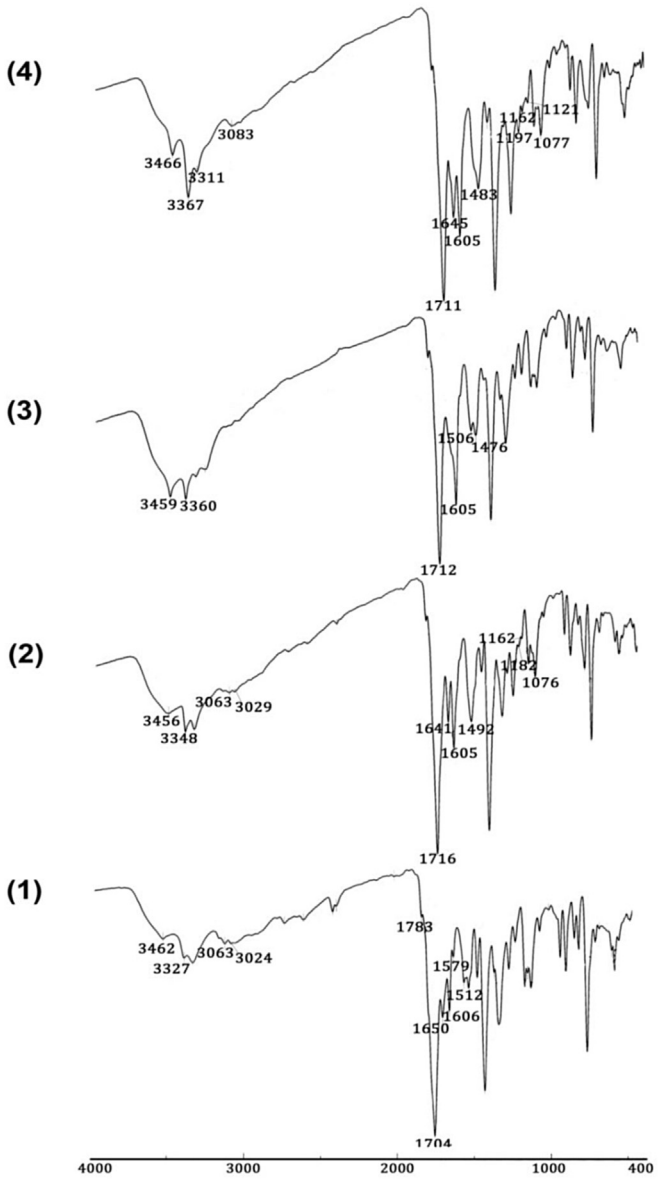


Fig. 1. Transmittance FTIR spectra of phthalimido aromatic hydrazide derivatives.

3.2. Antibacterial activity of the phthalimido aromatic hydrazide derivatives

Phthalimido aromatic hydrazide derivatives **1**–**4** were evaluated for their in vitro antibacterial activity against Gram-positive bacteria *B. subtilis* and *S. pneumoniae* and Gram-negative bacteria *E. coli* by the agar well diffusion technique using Ampicillin and Gentamicin as reference standards and the results are presented in Table 2.

Phthalimido aromatic hydrazide derivatives **1**–**4** showed good antibacterial activity. Their inhibitory effect against all the tested bacteria followed the sequence: **2** > **4** > **3** > **1**. The presence of hydroxyl group on the aromatic ring of the hydrazide part increased the antibacterial activity as evidenced by derivative **2**. Derivative **3** was less active than the derivative **2,** which indicates that the NH_2 group is less effective in improving the antibacterial activity than the hydroxyl group. The electron donating power of the amino group is larger than that of the hydroxyl group. This may increase the electron density on the amino derivative and consequently may decrease its potency to interact with the negatively charged microbial cell membrane leading to lower antibacterial activity compared to the hydroxy derivative. The lower antibacterial activity of derivative **4** in comparison to derivative **2** may be attributed to the presence of an additional NH_2 group in it. The non-substituted derivative **1** is the least active one among these derivatives against all the tested bacteria. The most active derivative **2** exhibited an inhibition zone diameter of 23.1 ± 0.63 mm with MIC value of 0.49 μg/ml (Table 2) against *S. pneumoniae* corresponded to the inhibition zone diameter of 21.6 ± 0.21 mm and MIC value of 0.98 μg/ml (Table 2) for standard drug Ampicillin. Thus, derivative **2** displayed better activity against *S. pneumoniae* than that of the reference drug Ampicillin. Moreover, derivative **4** showed activity against *S. pneumoniae* nearly equivalent to the reference drug Ampicillin (Table 2). The derivatives **1**–**4** showed greater antibacterial activity against *B. subtilis* than that against *S. pneumoniae.*

Moreover, the derivatives **1**–**4** were more active against the Gram-positive bacteria than against the Gram-negative bacteria (Table 2). As the strongest, derivative **2** caused inhibition zone diameter *of B. subtilis* and *S. pneumoniae* of 24.5 ± 0.67 and 23.1 ± 0.63 mm, respectively, corresponded to 21.3 ± 0.58 mm of *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, while 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 [39]. Therefore, these derivatives had different effects on the two kinds of bacteria. An additional evidence of the greater activity of these derivatives against Gram-positive bacteria than Gram-negative bacteria comes from their MIC values. Because the MIC values of the derivative **2** against *B. subtilis* and against *S. pneumoniae* were 0.24 and 0.49 μg/ml, respectively, the MIC value against *E. coli* was 3.9 μg/ml (Table 2).

3.3. Antifungal activity of the phthalimido aromatic hydrazide derivatives

Phthalimido aromatic hydrazide derivatives **1**–**4** were evaluated for their in vitro antifungal activity against *G. candidum*, *A. fumigatus*, and *S. racemosum* by the agar well diffusion technique using Amphotericin B as reference drug and the results are presented in Table 3.

It can be noted that, derivative **2** exhibited equivalent inhibition zone diameter (22.9 ± 0.44 mm) and MIC value (0.98 μg/ml) to the reference drug Amphotericin B (22.8 ± 0.11 mm, 0.98 μg/ml) against *A. fumigatus*. Further, derivative **2** emerged as the most potential candidates against *S. racemosum* with inhibition zone diameter of 21.2 ± 0.58 mm and MIC value of 0.98 μg/ml which are better than those of the standard drug Amphotericin B (20.3 ± 0.19 mm, 1.95 μg/ml). The rest of the derivatives exhibited different in vitro antifungal activity with inhibition zone diameter from 14.2 ± 0.63 to 21.4 ± 0.58 mm with MIC values from 0.98 to 125 μg/ml against the tested strains of fungi.

3.4. Thermal stability of the phthalimido aromatic hydrazide derivatives

Fig. 3 shows the results of the thermal stability and degradation behavior of the prepared phthalimido aromatic hydrazide

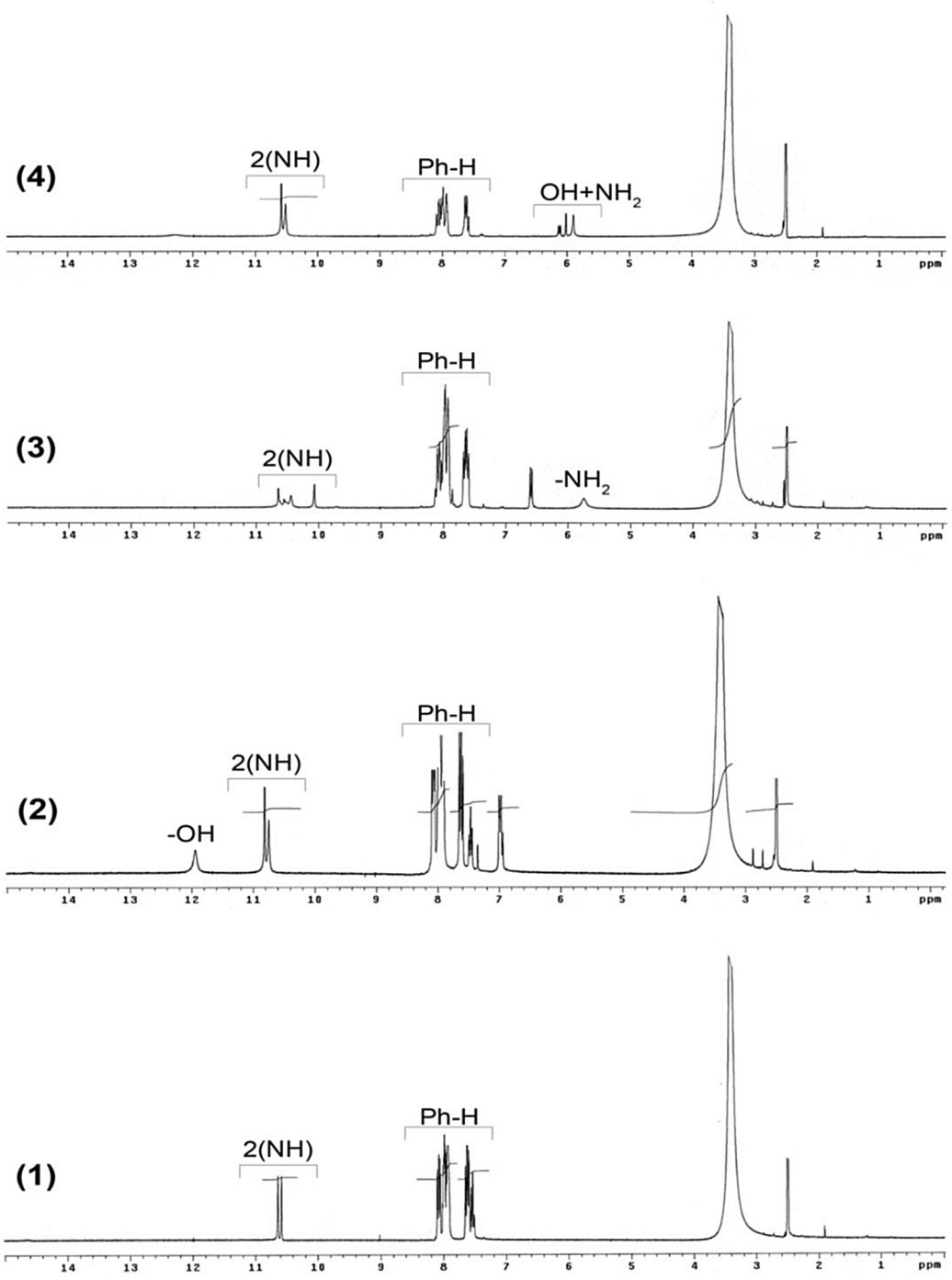


Fig. 2. ^{1}H NMR spectra of phthalimido aromatic hydrazide derivatives.

derivatives containing −OH and/or $-NH_2$ groups in the aromatic ring of their hydrazide part. These results illustrate the weight losses of these derivatives obtained from thermogravimetric analysis (TG) measurements in nitrogen atmospheres. TG measurements were performed on these derivatives in order to examine the influence of their structure differences on their degradation behavior. All the TG measurements were carried out at a heating rate of 10 °C min^{-1} and under a gas flow stream of 30 ml min^{-1}.

The results clearly revealed that all the investigated derivatives exhibited a characteristic similar degradation behavior which consisted of three distinct steps in which appreciable weight losses were detected. During the first weight loss step, which occurred between 90 and 130 °C, all the derivatives exhibited relatively small losses of only about 1–2.5% of their original weights. These weight losses were clearly attributable to the evaporation of absorbed moisture from the surface of the derivatives. The second step - in which all the investigated derivatives showed considerable losses - occurred in various temperature regions for various derivatives (Table 4). This step reflected the occurrence of the thermally induced cyclodehydration reaction of these derivatives into the

Table 2
Inhibition indices and minimum inhibitory concentration (MIC) of phthalimido aromatic hydrazide derivatives against *B. subtilis, S. pneumoniae and E. coli.*

Derivative code	Tested bacteria					
	B. subtilis (R CMB010069)		*S. pneumoniae* (R CMB 010019)		*E. coli* (RCMB 010055)	
	Inhibition zone (mm)	MIC (μg/ml)	Inhibition zone (mm)	MIC (μg/ml)	Inhibition zone (mm)	MIC (μg/ml)
1	18.3 ± 0.58	7.81	16.8 ± 0.58	15.63	14.2 ± 0.58	125
2	24.5 ± 0.67	0.24	23.1 ± 0.63	0.49	21.3 ± 0.58	3.90
3	20.3 ± 0.58	1.95	19.3 ± 0.44	3.90	16.8 ± 0.58	15.65
4	22.4 ± 0.63	0.49	21.3 ± 0.44	0.98	19.1 ± 0.25	3.90
Ampicillin	29.8 ± 0.15	0.015	21.6 ± 0.21	0.98	–	
Gentamicin	–	–	–	–	22.8 ± 0.22	0.98

Table 3
Inhibition indices and minimum inhibitory concentration (MIC) values of phthalimido aromatic hydrazide derivatives against *G. candidum*, *A. fumigatus*, and *S. racemosum.*

Derivative code	Tested fungi					
	G. candidum (RCMB 05098)		*A. fumigatus* (RCMB 02569)		*S. racemosum* (RCMB 05925)	
	Inhibition zone (mm)	MIC (μg/ml)	Inhibition zone (mm)	MIC (μg/ml)	Inhibition zone (mm)	MIC (μg/ml)
1	15.9 ± 0.58	31.25	15.2 ± 0.58	62.50	14.2 ± 0.63	125
2	23.9 ± 0.58	0.49	22.9 ± 0.44	0.98	21.2 ± 0.58	0.98
3	18.4 ± 0.44	7.81	17.1 ± 0.44	15.63	16.2 ± 0.63	31.25
4	21.4 ± 0.58	0.98	20.3 ± 0.55	1.95	18.9 ± 0.63	3.90
Amphotericin B	26.7 ± 0.15	0.12	22.8 ± 0.11	0.98	20.3 ± 0.19	1.95

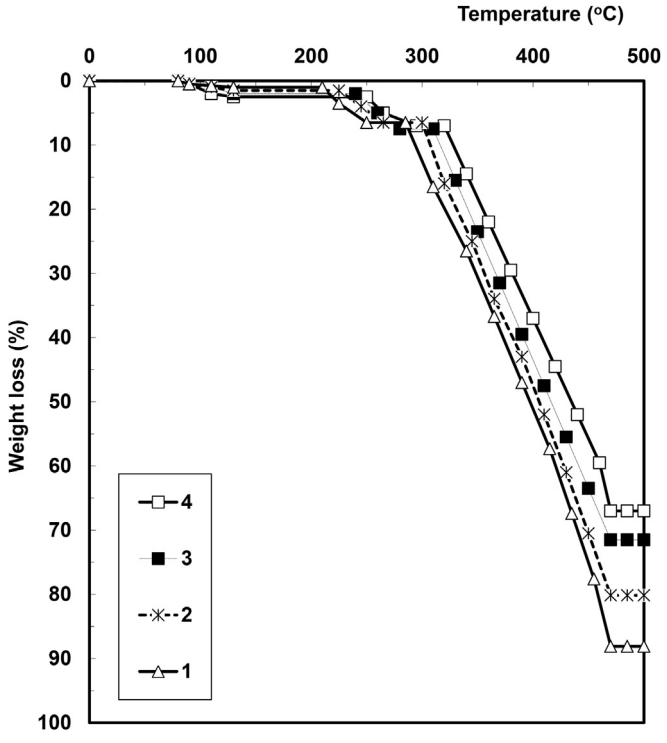


Fig. 3. Typical TG thermograms patterns of novel phthalimido aromatic hydrazide derivatives. All the thermograms were recorded in nitrogen, at a heating rate of 10 °C min^{-1} and under a gas flow rate of 30 ml min^{-1}.

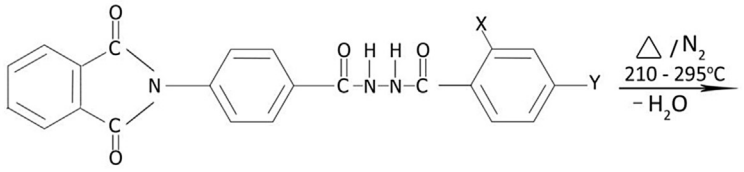
corresponding 1,3,4-oxadiazole derivatives (1′, 2′, 3′ and 4′) by losing water (Scheme 2). The amount of water evolved during the cyclodehydration reaction was 4.5–5.5% (based on the weight of the perfectly dried derivatives), which seems to be in good agreement with the theoretical value (4.33–4.68 wt %) calculated for the expected 1,3,4-oxadiazole derivatives (Scheme 2).

The third weight loss step was steep and indicated the decomposition of these derivatives containing 1,3,4-oxadiazole ring which were formed in the second step. It is worth mentioning that all of these losses were estimated relative to the samples' weights at the beginning of each step. As can be seen from Fig. 3, improved resistance to high temperatures was associated with the presence of –OH and/or $-NH_2$ groups in the investigated derivatives. Thus, at all used temperatures, the hydroxy amino derivative **4** showed the highest stability, relative to that of the other derivatives, as judged by the lowest weight losses and by the highest initial decomposition temperature. On the other hand, the derivative **1** (non-substituted one) exhibited the lowest thermal stability. The other derivatives aligned themselves in between these two extreme cases, so that with respect to their weight remaining at any particular temperature, their order of stability was **4** > **3** > **2** > **1**. Thus, –OH and/or $-NH_2$ substitution at the aromatic ring of the hydrazide part of these derivatives improved their stability at high temperatures. This should allow for establishment of stronger intermolecular hydrogen bonds which would be more difficult to break and therefore more resistance to elevated temperatures. The resulting 1,3,4-oxadiazole derivatives (1′, 2′, 3′ and 4′) start degradation in the temperature range above 285–320 °C without weight loss at lower temperature (Table 4). They lost 60–81.6% of their original weights at 500 °C. This high thermal stability may be attributed to the chemical structure of these derivatives which possesses an aromatic, an imide, a 1,3,4-oxadiazole rings, a phenolic –OH and/or aromatic $-NH_2$ groups. These groups are known to be highly resistance to elevated temperatures. This in addition to the strong intermolecular hydrogen bonding established between the imide carbonyl and the phenolic –OH and $-NH_2$ groups of the neighboring molecules.

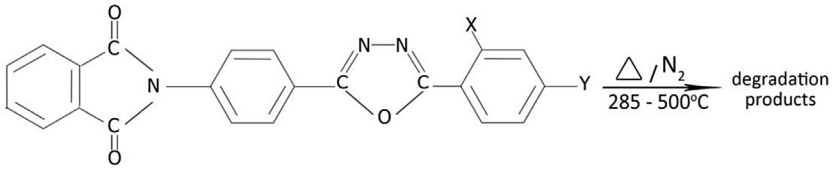
Table 4
Thermogravimetric analyses of novel phthalimido aromatic hydrazide derivatives, in nitrogen. Atmosphere at a heating rate of 10 °C min^{-1} and under a gas flow rate of 30 ml min^{-1}

Derivative code	Temperature range of cyclodehydration reaction/°C	Onset degradation temperature/°C	Weight loss/% at[a]		
			400 °C	450 °C	500 °C
1	210–250	285	44.50	68.50	81.60
2	225–265	300	41.00	64.00	73.66
3	240–280	310	36.00	56.00	64.00
4	250–295	320	30.00	48.75	60.00

[a] All the weight losses were determined relative to the derivatives' weights at the beginning of the degradation step.



Phthalimido aromatic hydrazide derivatives



Phthalimido aromatic -1,3,4 -oxadiazole derivatives

Derivative No.	**1′**	**2′**	**3′**	**4′**
X	H	OH	H	OH
Y	H	H	NH_2	NH_2

Scheme 2. Thermal cyclodehydration and decomposition reactions of novel phthalimido aromatic hydrazide derivatives.

3.5. Thermal stability of PVC in the presence of phthalimido aromatic hydrazide derivatives

Results of TG measurements of rigid PVC stabilized by various phthalimido aromatic hydrazide derivatives (**1**, **2**, **3** and **4**) are represented in Fig. 4. All the TG measurements were carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} and under a nitrogen flow stream of 30 ml min^{-1}. The results of the non-stabilized blank PVC and those of the PVC samples stabilized by dibasic lead carbonate (DBLC), barium-cadmium-zinc (Ba–Cd–Zn) stearate and n-octyltin mercaptide (n-OTM) as reference stabilizers are also given for comparison. The choice of these reference stabilizers was based on the fact that they represent the three major classes of the commercially used stabilizers, which are basic salt stabilizers, soap stabilizers and organtin stabilizers, respectively. For all the measurements, the stabilizers were used in a concentration of 2 wt % of PVC and the results represent the average of three comparable measurements of each stabilizer.

The results clearly revealed that the investigated derivatives exhibited a greater stabilizing efficiency than all the commercially used reference stabilizers. The greater stabilizing efficiency is shown not only by the higher initial decomposing temperature, but also by the higher rate of residual weights of PVC stabilized with the investigated derivatives during the subsequent stages of degradation as compared with the reference stabilizers (Fig. 4).

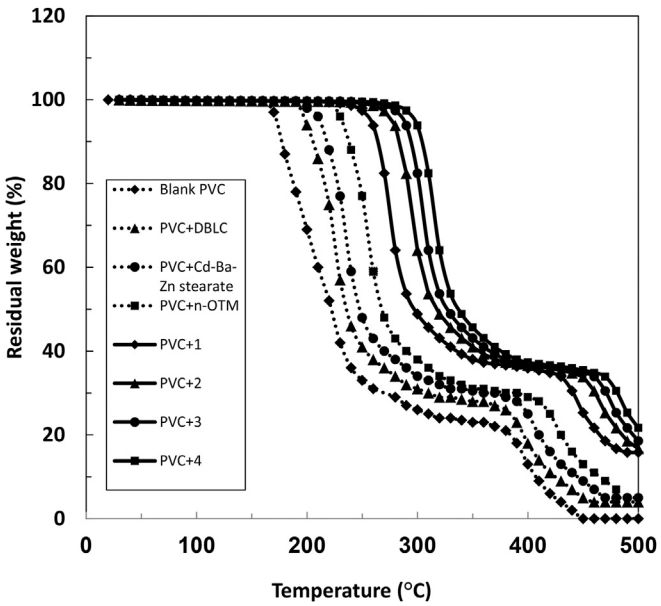


Fig. 4. Thermogravimetric curves of rigid PVC in the presence of 2 wt % of various phthalimido aromatic hydrazides derivatives and reference stabilizers at a heating rate of 10 °C/min and a nitrogen flow rate of 30 $mlmin^{-1}$.

Moreover, the results revealed that the nature of the substituent groups in the aryl nucleus of the hydrazide part (−OH and $-NH_2$ groups) of the investigated derivatives affects the initial decomposition temperature value to different extent, as well as the rate of the residual weight of the PVC stabilized with the phthalimido hydrazide derivatives. This indicates the important role played by the substituent groups at the aromatic ring in the stabilization process. The introduction of the −OH group and/or $-NH_2$ group into the phenyl rings resulted in to an appreciable increase in the initial decomposition temperature (at the early stages of degradation) and slight increasing in the residual weight (at subsequent stages of degradation). This may be attributed to the nature of these substituents (electron rich substituent), which could donate electrons towards the conjugated structure of the phthalimido aromatic hydrazides, increasing their ability to intervene in the degradation process of PVC relative to that of the non-substituted derivative **1**.

An experimental proof supporting this conclusion could be seen in the greater efficiency of the amino derivatives **3** and **4** relative to that of the hydroxy derivative **2**. This is in accordance with the greater electron donating power of $-NH_2$ group relative to that of the −OH group. The enhanced efficiency of the amino derivatives could also be related to another two reasons: (1) at the early stages of degradation, the presence of the amino group in the para-position in the phenyl ring may make its electron donation proceed to a greater extent and be much easier; and (2) the ability of the amino group to act as a HCl absorber at the subsequent stages of degradation based on its basic character, thus protecting the polymer from the deleterious effect of this acidic degradation promoter.

4. Conclusions

The prepared phthalimido aromatic hydrazide 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 compared with industrial stabilizers such as DBLC, Cd−Ba−Zn stearate and n-OTM. From the above conclusions, it is possible to recommend the use of phthalimido aromatic hydrazide derivatives as antimicrobial thermal stabilizers for rigid PVC, to obtain thermally stable antimicrobial PVC/phthalimido aromatic hydrazide composites.

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