

Stabilization of Poly(Vinyl Chloride) Against Photo-Degradation Using Dienophilic Compounds

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ABSTRACT: As dienophilic compounds, *N*-aminophenylmaleimides would be expected to act as radical traps and thus, could be investigated as organic photo-stabilizers for rigid poly(vinyl chloride) (PVC). Their stabilizing efficiencies were evaluated by measuring the extent of discoloration and the change in the mechanical properties of the photo-irradiated polymer. Their stabilizing efficiencies were compared with phenyl salicylate, which is a commonly used industrial photo stabilizer. The results have proved the higher stabilizing efficiency of all the investigated materials as compared with phenyl salicylate. The stabilizing efficiency of the aminomaleimides is attributed to their radical trapping potency which intervenes with the radical degradation of the photo-irradiated PVC. Moreover, it was found that these materials lower the extent of discoloration of the polymer during later stages of degradation. This improve-

ment in the color stability is most probably attributable to the ability of the aminomaleimides to react by a Diels–Alder reaction with the conjugated double bonds created on the polymeric chains as a result of the degradation of the polymer. Finally, the results illustrate the blending of aminomaleimide derivatives with phenyl salicylate improve the photo stabilization of the polymer as shown from the absorbance coefficient Δa values, and this improvement attains its maximum when both the investigated stabilizers and phenyl salicylate are taken in equivalent ratios. The observed synergism is attributed to the combination of the mechanisms by which both stabilizers function. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3218–3228, 2009

Key words: poly(vinyl chloride); photodegradation; extent of discoloration; mechanical properties

INTRODUCTION

The low cost and good performance of poly(vinyl chloride), PVC, make it one of the most important commercial thermoplastic polymers. It stands second in the world after polyolefins concerning the production and consumption of a synthetic material. However, PVC suffers from thermal and photo degradation. During degradation process two immediate and interrelated chemical effects are observed; Liberation of hydrogen chloride and development of intense coloration. Photodegradation gives rise to changes in the UV visible spectrum of the polymer due to the formation of conjugated polyenes as a result of dehydrochlorination.^{1–5} This process can be effected either chemically or thermally and photochemically.^{3–5} Because prerequisite for good performance of PVC in many applications is its resistance to sunlight. The fabrication of PVC into useful products occurred through molding process at 200°C. Thus, the addition of thermal stabilizers is always a must. Because the fabrication time is relatively short, measurements of the so-called residual

thermal stabilizer and determination of the consumed amount after various processing times indicate that considerable amount of the stabilizer remains in excess.^{6,7} Thus, the plastics formed contains large amounts of the unreacted heat stabilizer, the effect of which on the photo-degradation process may differ from its influence on thermodegradation. In this connection, photodegradation of PVC in presence of the commonly used tin^{8,9} or soap^{10,11} thermal stabilizers had been studied.

The mentioned classes of stabilizers are quite efficient at the industrial level but the metallic residue, from these organometallic compounds present serious environmental problems. Further, their by-products, mainly metal chlorides, accumulated during the reaction of these stabilizers with polymeric chains are considered as strong catalysts for the subsequent dehydrochlorination causing the sudden blackening of the polymer.^{12–14} Meanwhile, it is possible to struggle against these inconveniences using different types of metal-free photostabilizers. Recently, a new trend has been established based on the use of organic stabilizers for thermal stabilizers for rigid^{15,16} and plasticized PVC^{17,18} and as photostabilizers for rigid^{19,20} and plasticized PVC.^{21,22}

In previous work, aminophenyl maleimide derivatives had been investigated as metal-free, organic, thermal stabilizers for rigid PVC.^{23,24} The results

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revealed that the nitro aminophenyl maleimides are efficient thermal stabilizers, possessing the ability to act as powerful dienophiles which disrupt the polyene formation along the degraded PVC chains. It is therefore, worth studying the stabilizing efficiency of these products against photo-degradation of rigid PVC.

EXPERIMENTAL

Materials

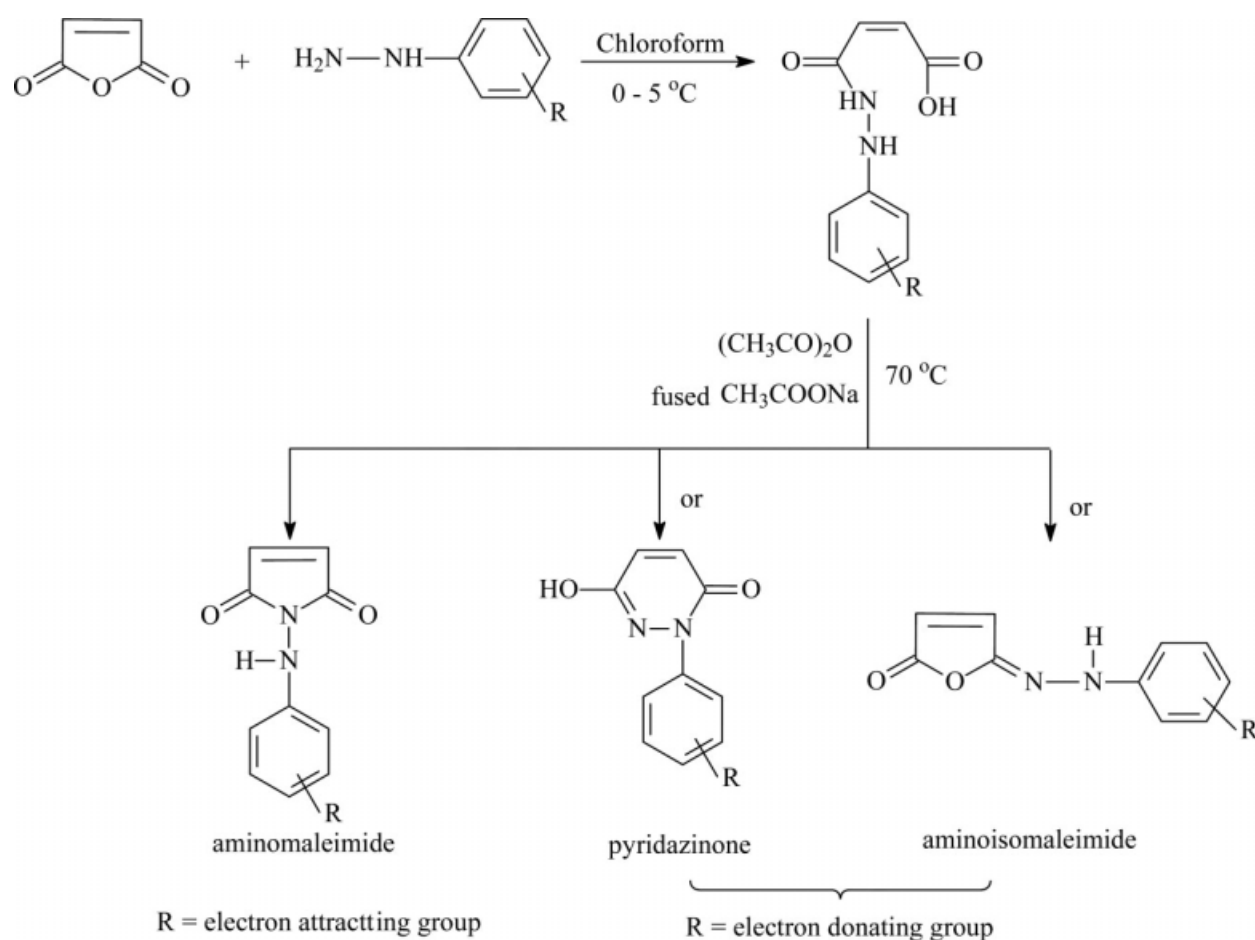
PVC (suspension) *K* value = 67 from National Plastic Company, (Sabic) Kingdom of Saudi Arabia and phenyl salicylate from El-Naser Company for Medic-

inal Chemicals, Egypt, were used for this investigation.

Tetrahydrofuran (THF) was obtained from Prolabo Company, France, analytical grade. It was refluxed over potassium hydroxide pellet for 3 h, and then distilled through a very short column.

Preparation of stabilizers

Various aminomaleimide derivatives listed in Table I, have been synthesized by two steps procedures according to the method described by Akasha and Mehta or Feuer.²⁵⁻²⁷ The course of the reaction²⁸ can be represented by the following equations:



The final products were confirmed by elemental analyses (Table I) and ¹³C-NMR spectroscopy (Figs. 1-3).

Preparation of PVC films

Films of PVC were prepared by dissolving the polymer (1 g) and the stabilizer (0.02 g) separately in

THF. The resulting solutions were then mixed, well stirred and poured into a petri-dish of known diameter. The films are formed on complete evaporation of the solvent at room temperature then heated in vacuum oven at 70°C to remove any residual THF (checked by the UV spectrum) the films were 0.2 ± 0.02 mm thick in all cases.

TABLE I
Analysis Data for the Prepared *N*-aminomaleimide Derivatives

Name <i>N</i> -(aminophenyl) maleimide	Abbreviation	m.p °C	Elemental analysis ^a			
			% C	% H	% N	% O ^b
<i>N</i> -(aminophenyl) maleimide	AMI	145	63.83 (63.82)	4.34 (4.28)	14.80 (14.89)	17.03 (17.00)
<i>N</i> -(amino 2-nitrophenyl) maleimide	2(-NO ₂)AMI	125	51.49 (51.51)	3.05 (3.03)	18.00 (18.02)	27.46 (27.45)
<i>N</i> -(amino 4-nitrophenyl) maleimide	4(-NO ₂)AMI	254	51.50 (51.51)	3.05 (3.03)	18.01 (18.02)	27.44 (27.45)
<i>N</i> -(amino 2,4-dinitrophenyl) maleimide	2,4-di (-NO ₂)AMI	175	43.16 (43.18)	2.20 (2.17)	20.10 (20.14)	34.54 (34.51)

^a Data given in parentheses correspond to the theoretical values.

^b Calculated as % O = 100 - (% C + % H + % N).

Photo-degradation

Photo-degradation was effected by $\lambda = 365$ nm ultra violet lamp from which the sample was held at a constant distance of 15 cm.

The film was preirradiated by a shorter wavelength $\lambda = 253$ for 10 min according to the method described by Torikai and Hasegawa,²⁹ because the main-chain scission of PVC and degradation product formation are accelerated under the longer wavelength radiation by preirradiation at shorter wave length.

Spectroscopic measurements

After photo-irradiation, the whole film is dissolved in THF in a given constant concentration for the UV/visible analysis using Perkin-Elmer-lambda 4-

UV/visible spectrophotometer. The rise in the absorbance coefficient Δa with the increase of irradiation time was determined for selected peaks according to Kaminska and Kaezmarek.³⁰

$$\Delta a = \frac{\Delta A}{d} = \frac{A_t - A_0}{d}$$

where, A_0 is the absorbance of nonirradiated sample, A_t is the absorbance of the same sample after irradiation time t and d (m) is the thickness of the PVC films.

Static mechanical measurements were performed on a zwick 1464 machine at room temperature (22°C) and a draw rate of 5 mm/min. The elasticity modulus (M), tensile strength (T) and relative elongation at break (E) % each value was the average of three measurements.

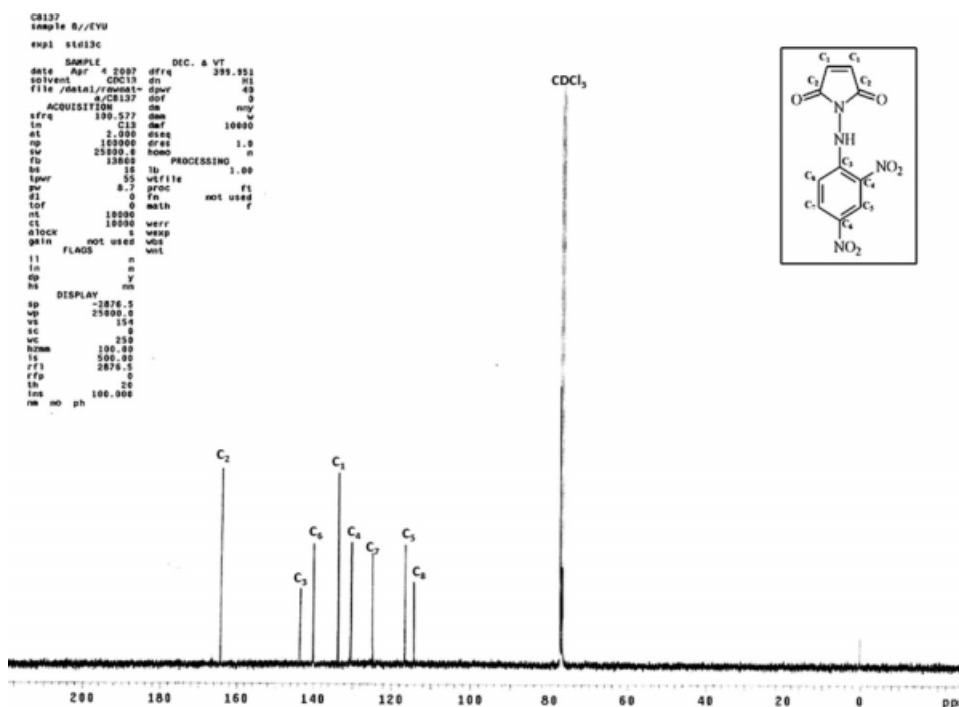


Figure 1 ¹³C-NMR spectrum of 2,4-di (-NO₂)AMI confirming the symmetrical structure of the condensation product.

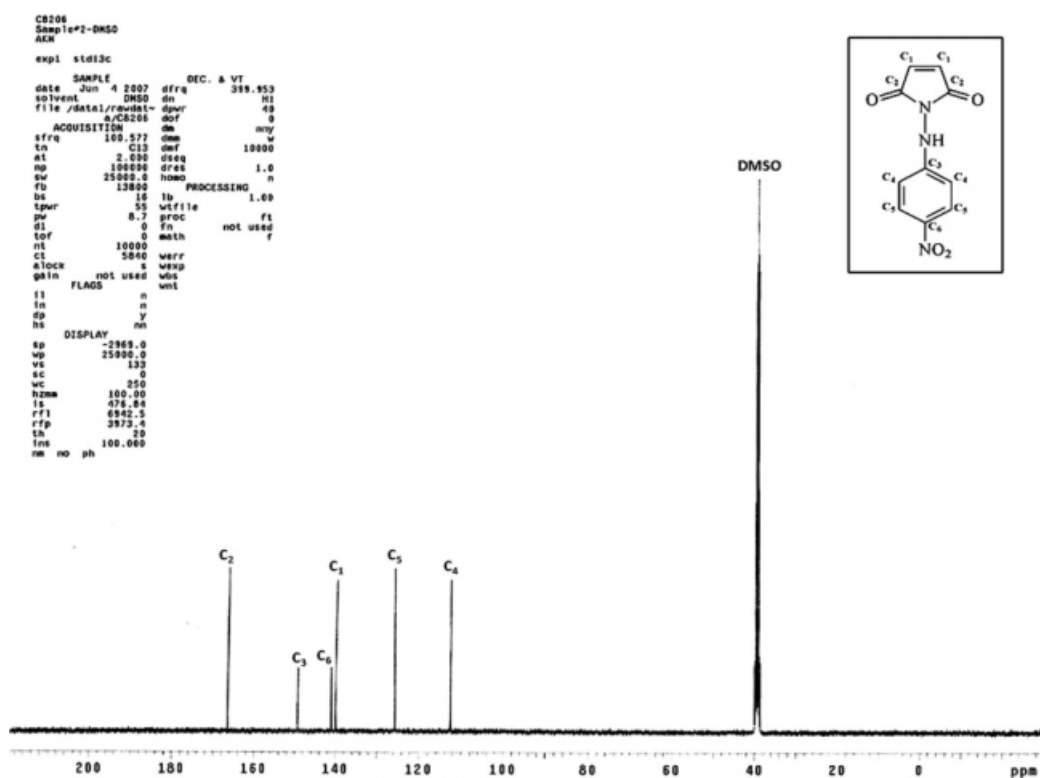


Figure 2 ^{13}C -NMR spectrum of *N*-(amino 4-nitrophenyl) maleimide confirming the symmetrical structure of the condensation product.

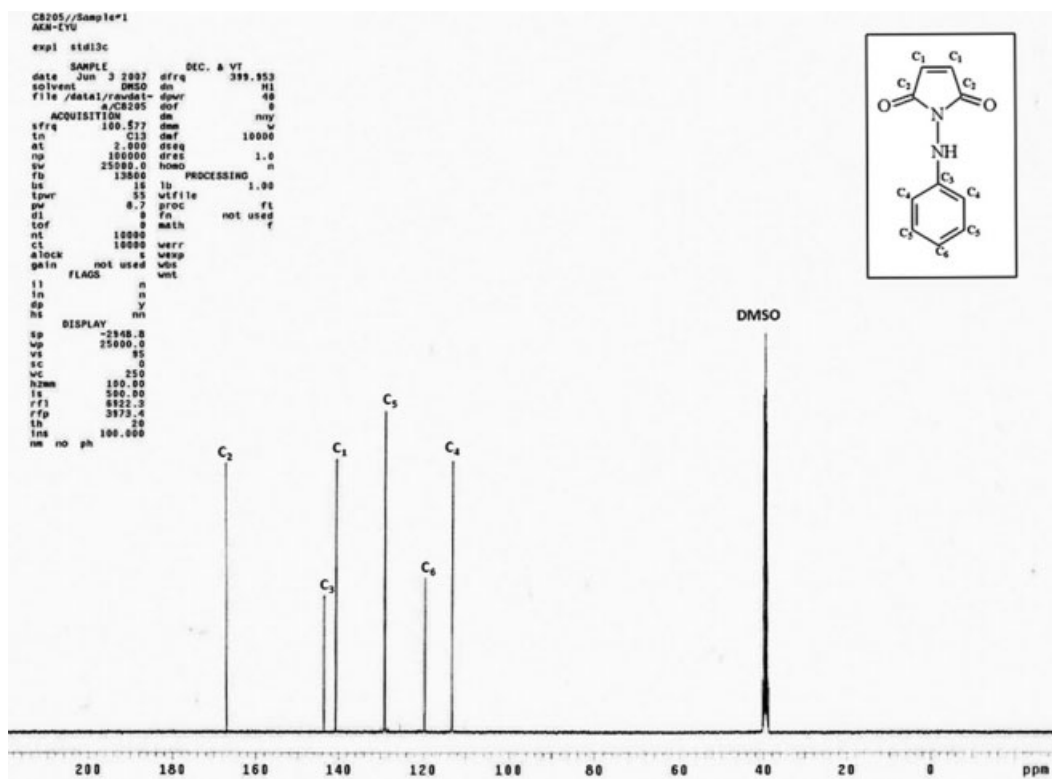
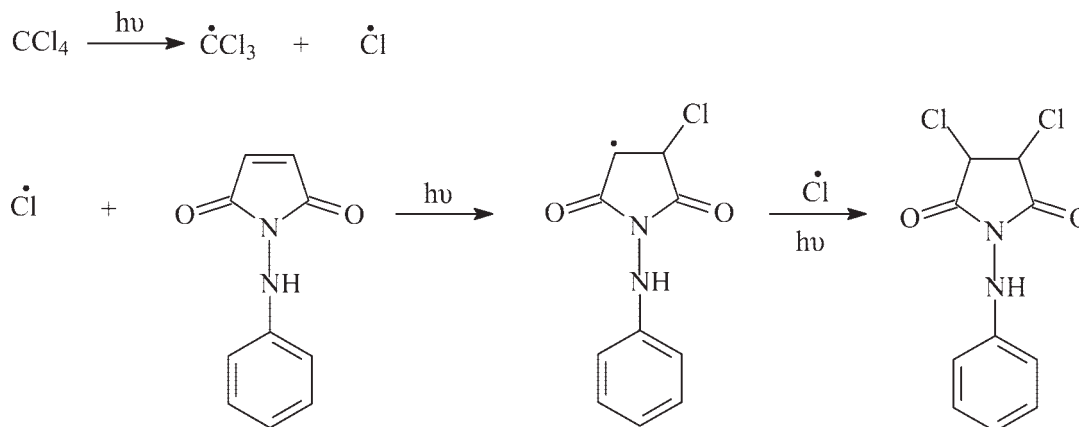


Figure 3 ^{13}C -NMR spectrum of *N*-(aminophenyl) maleimide confirming the symmetrical structure of the condensation product.

RESULTS AND DISCUSSION

Investigation of the ability of the aminomaleimides to act as radical traps

To investigate the ability of aminomaleimides to act as radical traps, the aminomaleimide derivatives were dissolved in carbon tetrachloride (a solvent which gives chlorine atoms on photolysis) and the



Elemental analysis	% C	% H	% N	% Cl
Theoretical	46.33	3.08	10.81	27.41
Found	46.28	3.12	10.86	27.32

Thus, the suggested material, as good radical traps, could be investigated as photo stabilizers.

Degradation of PVC samples in presence of aminomaleimides

In contrast to the pure polymer, which does not absorb ultraviolet radiation, the absorption spectra of the PVC films containing various aminomaleimide derivatives show characteristic well defined peak corresponding to the aminomaleimide derivative (Fig. 4).

The changes in the ultraviolet spectrum of pure PVC irradiated in air at different time intervals are illustrated in Figure 5. Several new absorption bands are observed, located at 313, 330, 368, 394, and 421 nm as compared with parent PVC. According to Starnes,³¹ the spectra shown in Figure 5 correspond to the formation of polyene sequences $-(\text{CH}=\text{CH})_n-$ $n = 4, 5, 7, 8,$ and 9 respectively. The relationship between the absorbance coefficient $\Delta a = (A_t - A_o)/d$ and the irradiation time t of PVC films containing aminomaleimide derivative (0.02 g/1 g PVC) are illustrated in Figure 6. Because d , (the thickness of film) is kept constant for all PVC films, the equation could be

solution was subjected to a low pressure UV lamp for 1 h. Benzophenone in a catalytic amount was added to enhance the radical decomposition of carbon tetra chloride. The elemental analysis has proved the presence of chlorine atom in the irradiated sample and it is in good accordance with the dichloro derivative of aminomaleimide as follows:

reduced to $\Delta a = \Delta A = (A_t - A_o)$ while, A_t = Absorbance of PVC film after time t , A_o = Absorbance of non-irradiated film. Figure 6 showed that PVC samples in

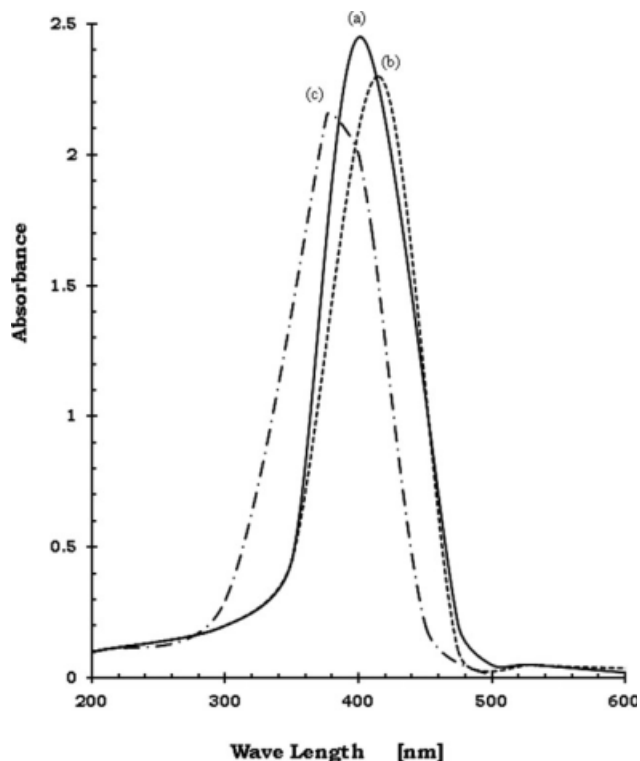


Figure 4 Absorption spectrum of PVC films containing AMI (a), 4(-NO₂)AMI (b), 2,4-di (-NO₂)AMI (c).

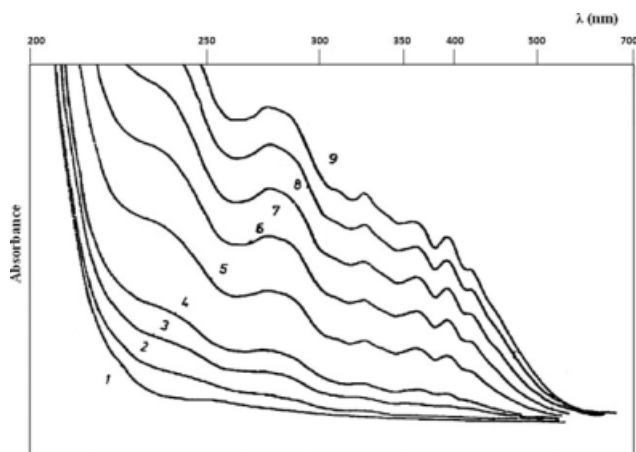


Figure 5 Absorbance of irradiated PVC film. Increasing absorbances correspond to successive increase in the irradiation time intervals.

presence of various aminomaleimide derivatives possessed lower Δa value than the reference UV stabilizer, phenyl salicylate, for a given irradiation time interval.

Thus, the all suggested materials possessed higher stabilizing efficiency than phenyl salicylate. The results in Figure 6 showed gradual increase in the Δa value at the early stages of degradation followed by a decrease in the Δa value which may be attributed to the ability of the aminomaleimide to act

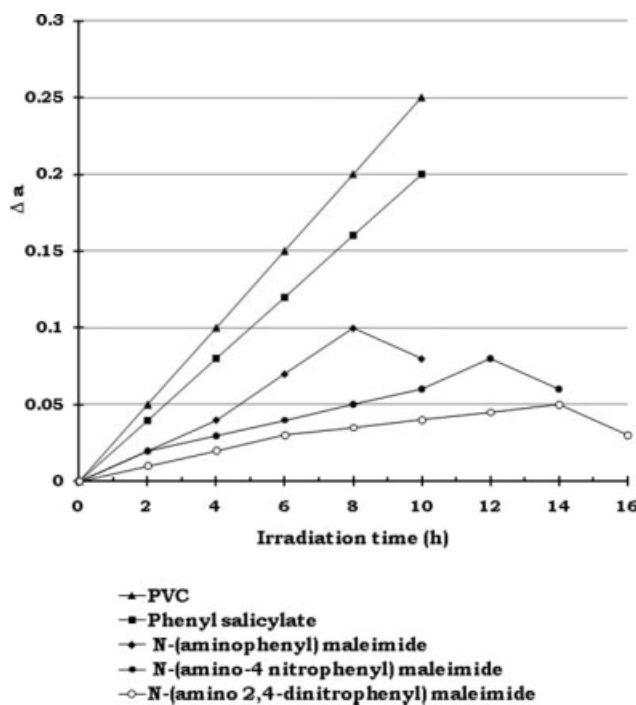


Figure 6 Change of absorbance coefficient of PVC film (1 g) with irradiation time in presence of various amino maleimide derivatives (0.02 g) as compared with the PVC film in presence of phenyl salicylate at $\lambda = 421$ nm (the samples concentrations are 0.02 g in 10 mL THF).

as powerful dienophile disrupting the polyene sequence through Deils-Alder reaction, leading to a decrease in Δa value. Moreover among the aminomaleimide derivatives, the *N*-(amino 2,4- dinitrophenyl) maleimide possessed the higher photostabilization efficiency as shown from the lowest Δa value. The unsubstituted aminomaleimide possessed the lowest photo stabilization efficiency whereas the mono nitro derivative, 4- nitro aminomaleimide, possessed intermediate efficiency. These results demonstrate the dependence of the stabilizing efficiency on the nitro group as an electron attracting group. The UV/Vis spectra of PVC films irradiated for 10 h in presence of various type of the suggested materials (0.02 g of stabilizer/1g PVC) are illustrated in Figure 7. Each irradiated film was dissolved in THF and precipitated in methanol to get rid of any residual unreacted stabilizer and then redissolved in THF for the UV analysis. Only the polyene sequence could be observed in the spectrum of the PVC sample in presence of AMI. This again a proof of the efficiency of the nitro group.

A mechanism for the stabilizing action of aminomaleimide derivatives on PVC films exposed to photo irradiation is illustrated in Scheme 1. The proposed mechanism is consistent with the following observations:

1. Complete dissolution of the irradiation PVC in presence of the suggested materials indicating the absence of crosslinking structures.
2. The elemental analyses of PVC films stabilized with various aminomaleimide derivatives and photo-irradiated at various time intervals up to 10 h after their dissolution in THF and reprecipitated in methanol to get rid of any residual stabilizers showed the presence of nitrogen

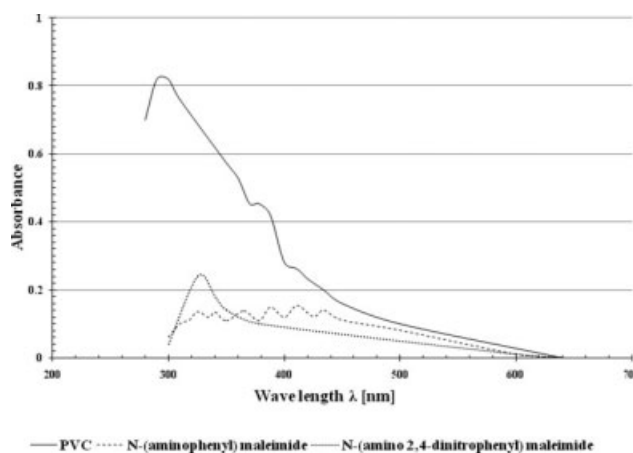
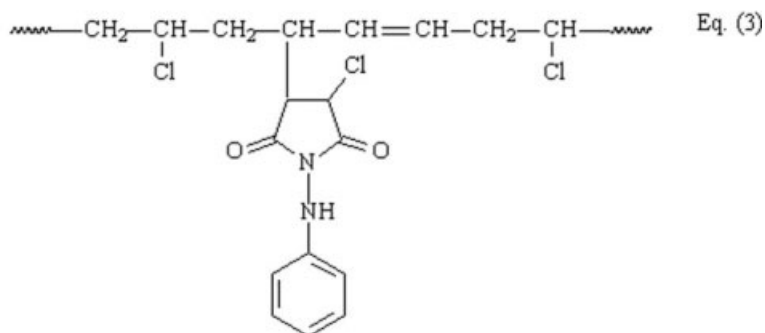
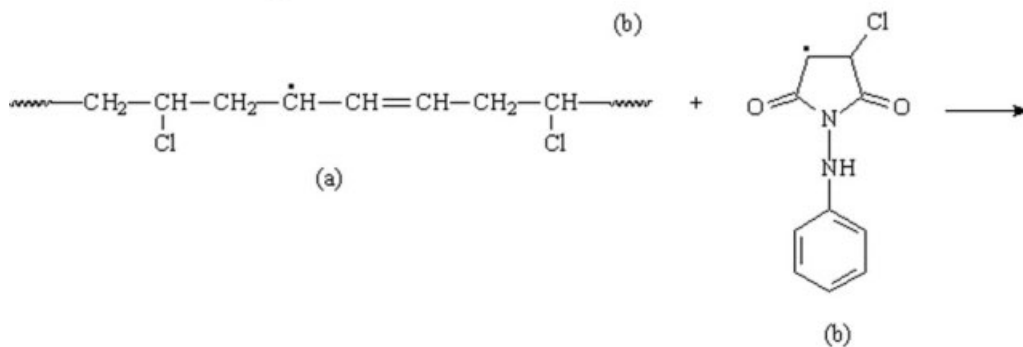
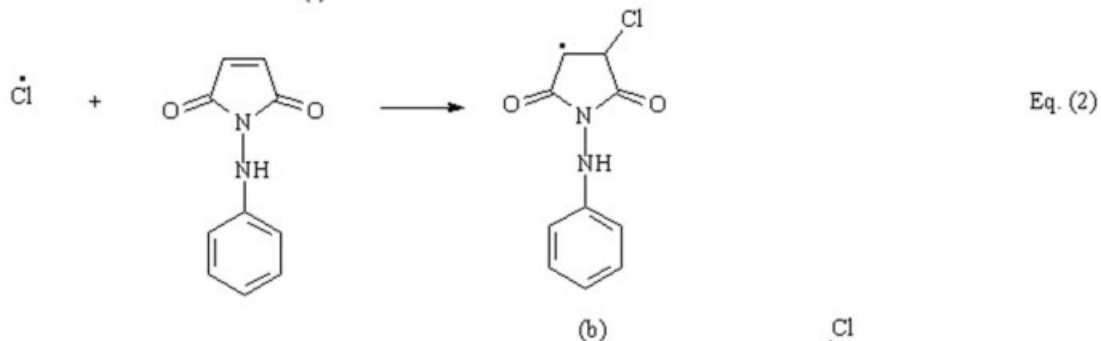
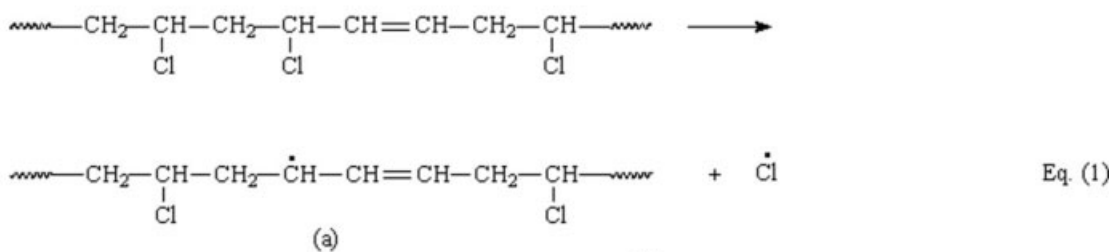


Figure 7 UV/visible spectra of PVC films in the presence of various type of amino maleimides after photo-irradiation in air for 10 h. The samples concentration are 0.02 g/10 mL.

a) at early stages of degradaton:



Scheme 1 Mechanism of stabilizing action of amino maleimide derivatives on PVC films exposed to photo irradiation.

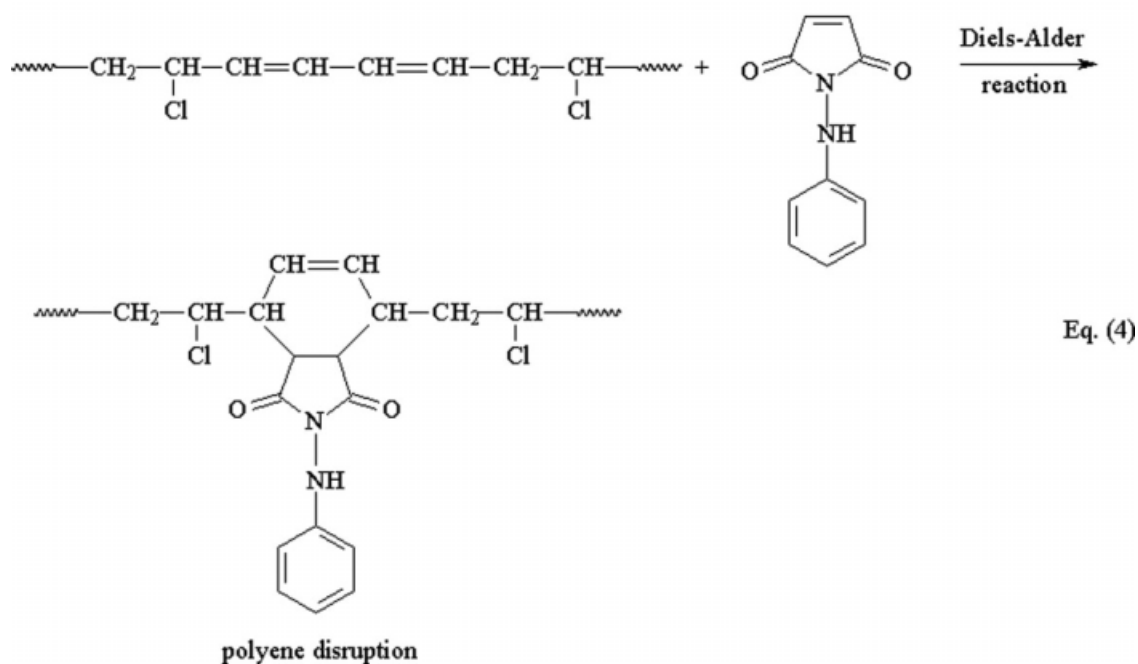
indicating the incorporation of the stabilizer into the polymeric chains [eqs. (1–3)].

- At the early stage of degradation, increasing the irradiation time for PVC films in presence of aminomaleimides led to lower Δa values as compared with that in the case of non stabilized PVC. Moreover, at the later stage of degradation. A distinguished decrease in the Δa value indicating the disrupt of polyene sequences through Diels–Alder reaction [eq. (4)].

Effect of aminomaleimide derivatives on the mechanical properties of photo-irradiated PVC films

The high stabilizing efficiency of the aminomaleimides can be additionally proved by evaluating their effects on the mechanical properties of photo irradiated rigid PVC films, for various time intervals as registered in Table II. The results for the nonstabilized blank sample and the sample stabilized by phenyl salicylate as reference photo stabilizer are

(b) In case of the presence of any conjugated polyenes at later stages of degradation:



Scheme 1 (Continued from the previous page)

also given for comparison. In all cases, the stabilizers were used at constant concentration (0.02 g/1 g PVC) and the result represent the average of three comparable runs for ultimate tensile strength (T), Young's modulus (M) and elongation at break (%) (E). It can be seen from Table II that the PVC films stabilized with the aminomaleimides showed greater retention of their mechanical properties [M, E (%) and T] relative to the sample stabilized with phenyl salicylate. These results indicate the proposed mechanism which gives predominance, at the early stages of degradation, to the interaction of the ethylenic double bond of the nitro aminomaleimide molecule with the chlorine atoms splitting from the polymeric

chains and consequently blocks the odd electron sites on PVC chains and the ability of the ethylenic double bond to act as powerful dienophiles at the later stages of degradation. Thus preventing or at least minimizing any possibility of conjugated double bond formation, chains-cission and crosslinking of PVC molecules avoiding drastic change in the mechanical properties of the polymer.

Effect of mixed stabilization on the photo-stabilization of PVC

In the aforementioned mechanism of stabilization of photo-irradiated rigid PVC in the presence of

TABLE II
Effect of Various Aminomaleimide Stabilizers on the Mechanical Properties of Photo Degraded Rigid PVC

Stabilizer used	Mechanical properties (M/E/T) ^a Degradation time (h)			
	0	4	8	12
Blank PVC	420/18/29	450/16/34	490/13/36	520/9/40
Phenyl salicylate	420/18/29	431/17/32	440/16/34	465/13/37
AMI	420/18/29	429/17/31	435/16/33	450/14/36
4(-NO ₂)AMI	420/18/29	420/18/29	427/18/28	445/16/33
2,4-di (-NO ₂)AMI	420/18/29	420/18/29	420/18/29	427/17/30

^a M, elastic modulus (N mm⁻²); E, elongation at break (%); T, tensile strength (N mm⁻²).

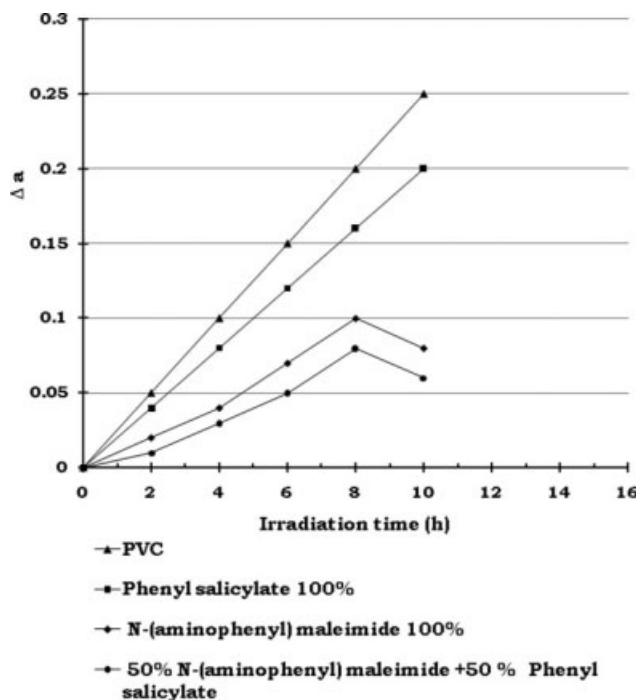


Figure 8 Change of absorbance coefficient of PVC film (1 g) with irradiation time in presence of AMI (0.02 g) as compared with the PVC film in presence of phenyl salicylate at $\lambda = 421$ nm (the samples concentrations are 0.02 g in 10 mL THF).

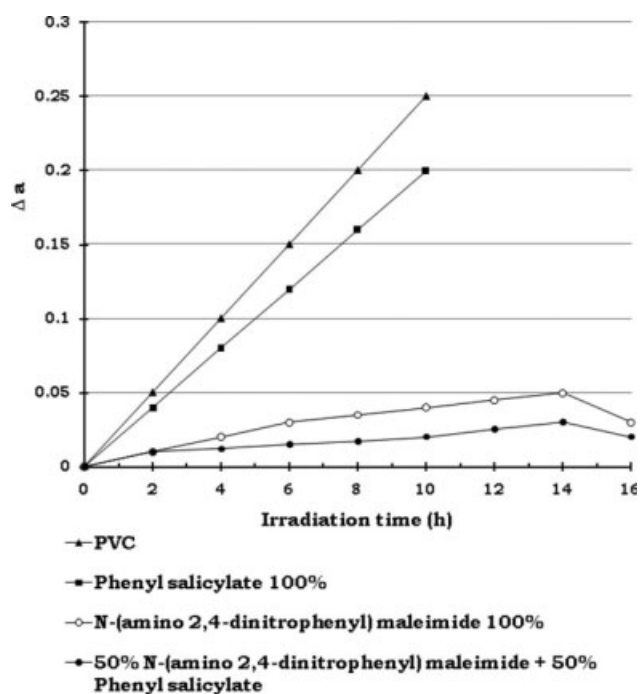


Figure 10 Change of absorbance coefficient of PVC film (1 g) with irradiation time in presence of 2,4-di(NO₂)AMI (0.02 g) as compared with the PVC film in presence of phenyl salicylate at $\lambda = 421$ nm (the samples concentrations are 0.02 g in 10 mL THF).

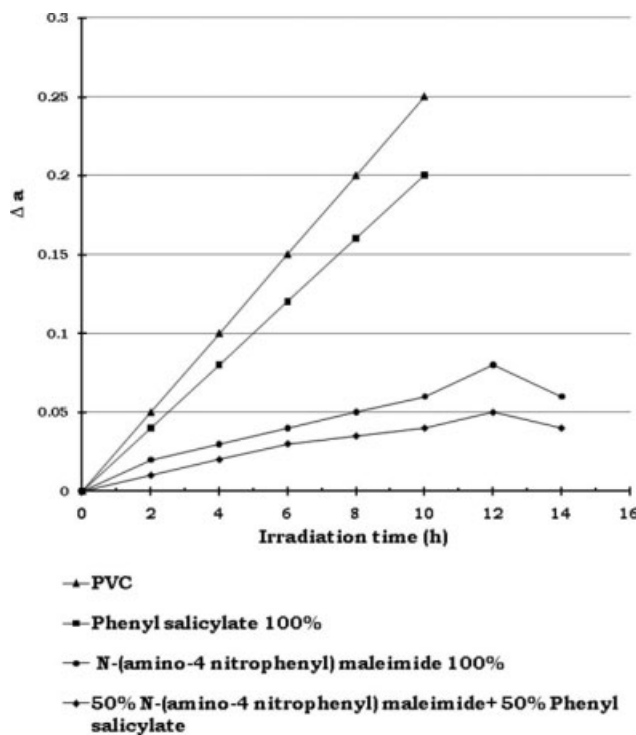


Figure 9 Change of absorbance coefficient of PVC film (1 g) with irradiation time in presence of 4-(NO₂)AMI (0.02 g) as compared with the PVC film in presence of phenyl salicylate at $\lambda = 421$ nm (the samples concentrations are 0.02 g in 10 mL THF).

various aminomaleimide derivatives, it was suggested that the stabilizing action of these materials involves a radical mechanism which disrupts the radical degradation process of the polymer through blocking the odd electron sites created on PVC chains. However, Phenyl salicylate is known to be UV absorber. Thus mixing of these two types of stabilizers might lead to complementary action. Accordingly, the stabilizers under investigation were mixed with phenyl salicylate. Mixing was effected in the ranges 0–100% of aminomaleimide derivative relative to the reference stabilizer. The overall mixed stabilizer concentration was kept 0.02 g/1 g PVC, and the results represent the average of three comparable experiments. The results showing the relationship between Δa and the irradiation time for PVC film stabilized with the aminomaleimide stabilizer mixed with phenyl salicylate are illustrated in Figures 8–10.

The results clearly indicate the lower Δa value of the mixed stabilizers as compared with each stabilizer individually, indicating the existence of a synergistic effect resulting from the combination of the aminomaleimide stabilizer with the reference one, the maximum synergism was achieved when both stabilizer were mixed in equivalent ratios as shown from Figures 11–13. PVC samples in presence of the mixed stabilizers retain the nitro aminomaleimide

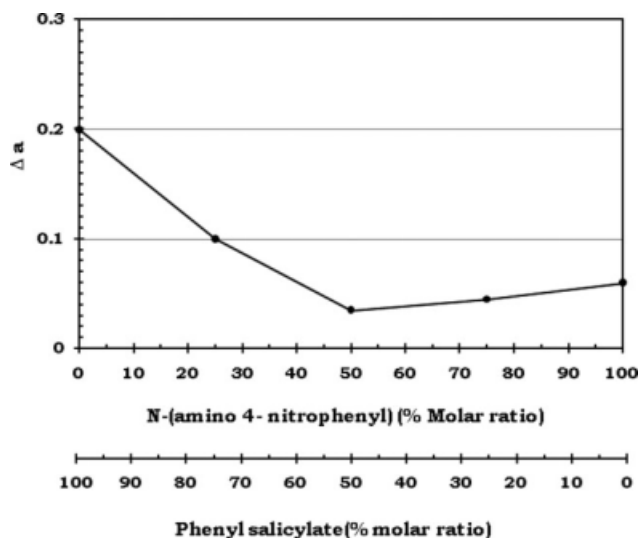


Figure 11 Extent of discoloration of photo-irradiated rigid PVC for 10 h, in the presence of various molar ratios of *N*-(amino 4-nitrophenyl) maleimide mixed with phenyl salicylate.

behavior which shows gradual increase in the Δa value at the early stages of degradation followed by decrease in Δa value at the later stages of degradation indicating the disruption of polyenes sequences through Diels–Alder reaction. However the presence of phenyl salicylate as UV absorber could delay the start of photodegradation for some irradiation time after which the action of aminomaleimide stabilizer will start. Thus both stabilizer possessed complementary function which could explain the synergism between them (Figs. 11–13).

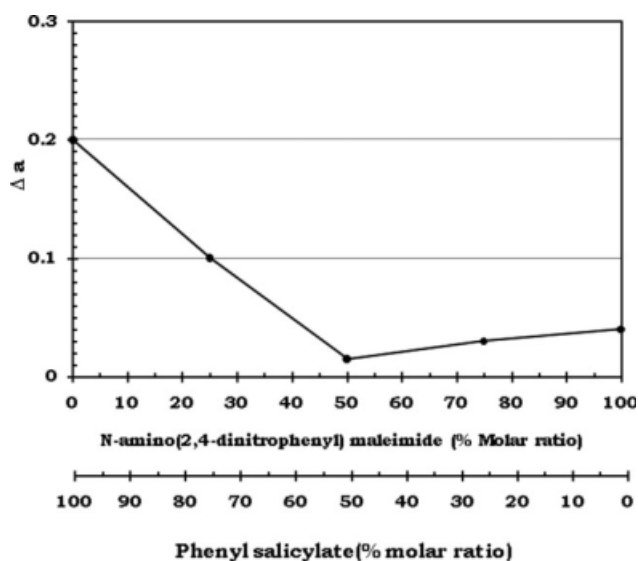


Figure 12 Extent of discoloration of photo-irradiated rigid PVC for 10 h in the presence of various molar ratios of *N*-amino(2,4-dinitrophenyl) maleimide mixed with phenyl salicylate.

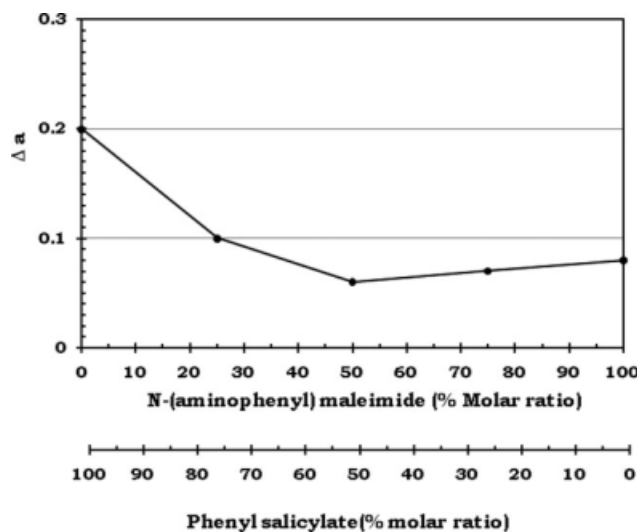


Figure 13 Extent of discoloration of photo-irradiated rigid PVC for 10 h in the presence of various molar ratios of *N*-(aminophenyl) maleimide mixed with phenyl salicylate.

CONCLUSIONS

1. *N*-aminomaleimide derivatives are efficient photo-stabilizers for rigid PVC as compared with the commonly used industrial phenyl salicylate UV absorber. The investigated materials exhibited their high stabilizing efficiency both through the replacement of the labile chlorine on the PVC chains by more stable stabilizer moieties and their ability to act as powerful dienophiles.
2. Their stabilizing efficiencies are significantly influenced by the presence of nitro group as substituent in the phenyl ring being the greatest (lower Δa value) for 2,4-dinitro derivative and the lowest (higher Δa value) for the unsubstituted (absence of nitro group) derivative.
3. Moreover, the PVC sample in presence of the investigated materials showed greater retention of their mechanical properties relative to the PVC sample in presence of the reference stabilizer.
4. Blending *N*-aminomaleimide derivatives stabilizers with phenyl salicylate leads to a remarkable decrease in Δa value. The greater effect is reached at an equivalent weight ratio of the components. The observed synergistic effect is most probably attributed to the combination of the mechanisms by which the aminomaleimides phenyl salicylate work.

From the above-mentioned data, one can recommend the use of *N*-aminomaleimide either as photo-stabilizers for rigid PVC or as costabilizers with phenyl salicylate for rigid PVC.

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