

Phenyl Urea Derivatives as Organic Stabilizers for Rigid Poly(vinyl chloride) against Photo-Degradation

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Received 11 September 2005; accepted 12 June 2006

DOI 10.1002/app.25205

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Phenyl urea derivatives have been prepared and investigated as photostabilizers for rigid PVC by measuring the extent of weight loss (%), the amount of gel formation as well as the intrinsic viscosity of the soluble fractions of the degraded polymer. Moreover, the efficiency of these stabilizers was evaluated from the extent of discoloration of the degraded polymer in their presence. The results indicated a reasonable stabilizing effect of these derivatives when compared with the commercially used UV stabilizers: phenyl salicylate (Salol) and methanone, 2-hydroxy-

4-(octyloxy)-phenyl-benzophenone. A synergistic effect is achieved when the phenyl urea derivatives are mixed with the UV absorbers in the ratio (75 : 25%), respectively. A radical mechanism is proposed to account for the stabilizing action of the products investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2217–2226, 2007

Key words: poly(vinyl chloride); UV absorbers; phenyl urea derivatives; intrinsic viscosity; gel content; weight loss; SEM

INTRODUCTION

A prerequisite for good performance of PVC in many applications is its resistance to sunlight.

Plastics in general are fabricated into useful products by operations that invariably involve heat stress (temperatures up to 200°C). Thus, heat stabilizers are usually added. For PVC, the time of fabrication is relatively short.

Measurements of the so-called residual thermal stability of PVC mixtures^{1–4} and determination of the amount of stabilizer consumed^{4,5} after various processing times indicate that most of the stabilizer remains unreacted. Thus, the final product contains large amounts of heat stabilizer, the effect of which on the photo-degradation process may differ substantially from its effect on thermo degradation.

In a previous work, phenyl urea derivatives have been investigated as thermal stabilizers or costabilizers⁶ for rigid PVC under air, at 180°C. The results reveal the higher stabilizing potency of the investigated organic stabilizers when compared with the commercially known reference stabilizers. It is, therefore, worth studying the stabilizing efficiency of these products against the photo-degradation of rigid PVC.

Recently, the focus of scientists was directed to the use of substituted maleimides and itaconimides^{7,8} as

photostabilizers for rigid PVC. Also they used glucoside derivatives as novel photostabilizers for rigid PVC.⁹ 5-Pyrimidine carbonitrile derivatives was also used as photo stabilizers for PVC.¹⁰ Also anthraquinone derivatives have been prepared and investigated as photostabilizers for rigid PVC.¹¹

EXPERIMENTAL

Materials

PVC (suspension) with a *K* value of 70 was supplied by Hüls Co. (Germany) and phenyl salicylate (Salol) from El-Nasr Company for Medicinal Chemicals, Egypt. Methanone, 2-hydroxy-4-(octyloxy)-phenyl-benzophenone was obtained from the "Linkers" Company—Far East Pte Ltd.—Singapore. Tetrahydrofuran (THF) solvent (analytical grade) was obtained from Prolabo Company, France. It was refluxed over potassium hydroxide pellets for 3 h and then distilled through a very short column. The pure solvent was stored in dark bottles and never used after more than 3 weeks from distillation, as fresh peroxides might be formed.

Preparation of the organic stabilizers

Preparation of phenyl urea derivatives

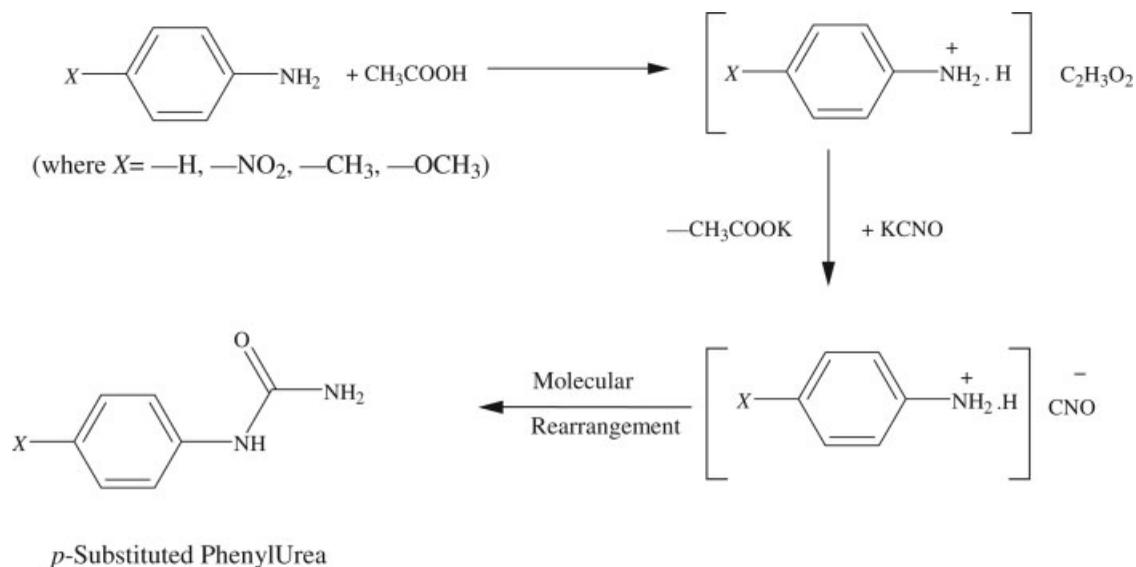
These materials were prepared according to the methods described by Vogel.¹²

Equimolar amounts of aniline (or *p*-substituted aniline) were dissolved in 10 mL glacial acetic acid diluted to 100 mL, contained in a 250-mL beaker; a solution of pure potassium cyanate was added, with

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stirring, to 50 mL of warm water. This was allowed to stand for 30 min, then cooled in ice and allowed to stand for another 30 min. It was filtered at the pump, washed with water, and dried in air oven.

Monophenyl urea was recrystallized from boiling water. The code names, melting points, and elemental analyses of the prepared materials are tabulated in Table I.



Preparation of PVC films

Films of PVC containing either the reference stabilizer or the material under investigation were prepared by dissolving the polymer and the stabilizer separately in THF. After complete dissolution, the two solutions were mixed and stirred to attain maximum homogeneity. The resulting solution was then poured into a Petri dish of known constant diameter. The films formed on complete evaporation of the solvent at room temperature were then immersed in diethyl ether, followed by heating in a vacuum oven at 70°C, to remove any residual THF.¹³ The films were 0.10 ± 0.02 mm thick in all cases.

Photo-degradation

Photo-degradation was affected by a 375-W PRK-2M type UV lamp covering the full range of the UV

region—from which the sample was held at a constant distance of 15 cm. The temperature around the sample was kept constant at 70 ± 2°C¹⁴ “to obtain effective results in a convenient time.”

Method of evaluation of the stabilizing efficiency

Weight loss measurements were carried out according to the following equation:

$$\text{Weight Loss (\%)} = (W_1 - W_2/W_1) \times 100$$

where W_1 is the weight of original sample (before irradiation), and W_2 is the weight of the sample (after irradiation).

The gel content of the degraded polymer samples was determined by dissolving constant weights (0.5 g) of each sample, photolyzed for various time intervals, in 20 mL THF at 35°C overnight. The insoluble

TABLE I
Physical Properties and Analyses Data for the Prepared Substituted Derivatives

Material	Code name	mp (°C)	Elemental analysis (calculated)			Elemental analysis (found)		
			C%	H%	N%	C %	H%	N%
Phenyl urea	Φ U	147	61.7	5.8	20.5	61.5	5.2	20.2
<i>p</i> -CH ₃ -phenyl urea	<i>p</i> -CH ₃ -ΦU	175	64.0	6.6	18.6	64.2	6.5	18.5
<i>p</i> -OCH ₃ -phenyl urea	<i>p</i> -CH ₃ O-ΦU	165	57.8	6.0	16.9	57.6	6.1	16.7
<i>p</i> -NO ₂ -phenyl urea	<i>p</i> -NO ₂ -ΦU	150	46.4	3.8	23.2	46.2	3.9	23.0

TABLE II
Measurements of Weight Loss, Soluble Fraction, Gel Content, and Intrinsic Viscosity for Rigid PVC in the Presence of Phenyl Urea Derivatives Acting as Photo Stabilizers, Compared with the Reference Stabilizers

Material	Weight loss (%)	Gel content (%)	Soluble fraction (%)	Intrinsic viscosity [η] (dL/g)
PVC (h)				
3	3.2	13.02	85	3.21
6	4.53	17.5	82	3.5
9	5.34	20.77	79	4.17
15	6.39	25.87	74.05	4.58
PVC + (A) (h)				
3	2.7	10.98	88.77	2.96
6	3.95	15.06	85	3.3
9	4.81	18.89	81.2	3.87
15	5.47	23.83	75.9	4.27
PVC + (B)				
3	2.36	8.77	91	2.74
6	3.43	12.85	86.87	3.12
9	4.38	16.43	83.22	3.6
15	5.13	21.7	78	3.97
Φ urea				
3	0.4	7.12	92.5	2.38
6	2.48	10.13	89	2.75
9	3.39	12.02	87.5	3
15	4.11	14.16	85	3.32
<i>p</i> -CH ₃ - Φ urea				
3	0.2	3.09	96.5	2.08
6	1.986	6.01	93.5	2.38
9	2.83	7.73	92.77	2.477
15	3.24	9.01	91	2.6
<i>p</i> -OCH ₃ - Φ urea				
3	0.3	4.55	95	2.16
6	2.15	7.38	92.5	2.49
9	3.05	9.27	90.47	2.62
15	3.52	10.73	89.11	2.8
<i>p</i> -NO ₂ - Φ urea				
3	0.35	5.75	94	2.26
6	2.29	8.67	91	2.61
9	3.22	10.56	89.5	2.78
15	3.79	12.36	86.87	3.01

A indicates phenyl salicylate (Salol); B, methanone, 2-hydroxy-4-(octyloxy)-phenyl-benzophenone. PVC (nonirradiated) $[\eta] = 1.6$.

fractions were then separated by centrifugation, washed with the solvent, and dried to constant weight in an air oven. The percentage gel was calculated as follows:

$$\% \text{ Gel} = W_2/W_1 \times 100$$

where W_1 is the weight of original sample, and W_2 is the weight of the insoluble fraction (gel fraction).

Moreover, the soluble fractions were precipitated in cold methanol, filtered, and dried, in an air-oven, to constant weight. The percentage of soluble fractions was then determined to be assured from the amount of gel previously determined.

$$\% \text{ Soluble fraction} = W_3/W_1 \times 100$$

where W_1 is the weight of original sample, and W_3 is the weight of soluble fraction after precipitation in methanol (after complete evaporation of solvent and complete dryness).

The viscosity measurements for the soluble fractions were carried out in a thermostated water bath on 1% solutions of the soluble fraction of polymer samples in DMF solvent at 30°C using a suspended-level Ubbelohde viscometer with negligible kinetic energy correction^{15,16} and which allowed dilution in the viscometer.

Scanning electron microscope analysis

Scanning electron microscope (SEM) analyses were performed by using the JEOL-JEM-100S electron microscope, Japan. Electric and magnetic lenses are used to focus electrons. The wavelength of the electrons, depending on their energy, is very short (about 0.086Å). Magnifications up to 250,000 times have been obtained. The accelerated voltage was 40 kV and the beam current was 40 μ A. Samples were coated with gold by using sputtering technique.

RESULTS AND DISCUSSION

Weight loss and gel formation as criteria for the photo-stabilizing efficiency of the investigated stabilizers

The results of the weight loss (%) as a function of the photoirradiation time are tabulated in Table II and represented in Figure 1. The results clearly reveal the low extent of weight loss of photodegraded PVC

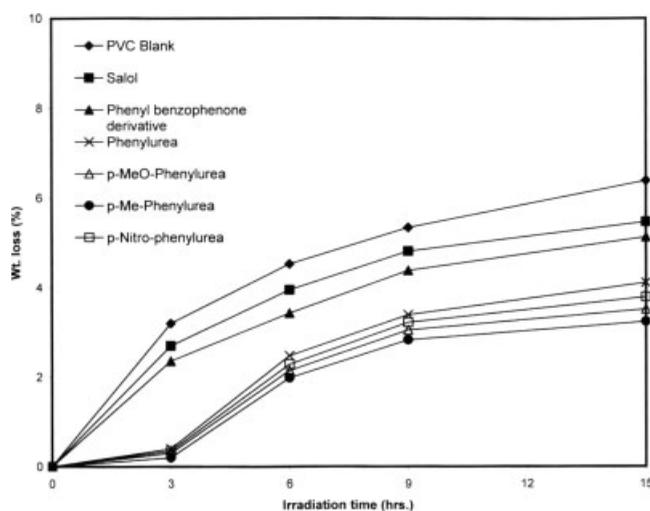


Figure 1 Variation of weight loss (%) for phenyl urea derivatives with irradiation time (h).

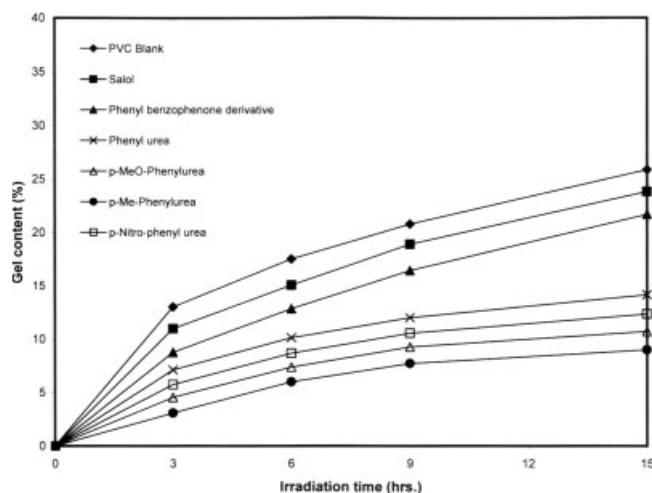
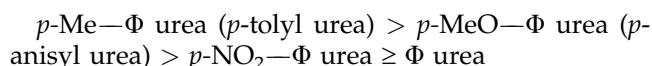


Figure 2 Variation of gel content (%) of phenyl urea derivative with irradiation time (h).

stabilized by phenyl urea derivatives when compared with the weight loss of photodegraded PVC and PVC stabilized by the two reference UV absorbers. This stabilizing efficiency of the investigated photostabilizers for the Φ urea derivatives was found to follow the following order:



The stabilizing efficiency of the investigated stabilizers is so pronounced that, for example in case of *p*-Me- Φ urea stabilizer (*p*-tolyl urea) (which gives the least % of weight loss), the weight loss percent of PVC degraded after 3 h of irradiation is only 6.25% that of the blank PVC, $\sim 7.4\%$ that of PVC stabilized with salol, and $\sim 8.47\%$ that stabilized with the hydroxy phenyl derivative of benzophenone stabilizer; while after 15 h of irradiation, the weight loss (%) of degraded PVC in the presence of *p*-Me- Φ urea was found to be equal to 50.7% that of the blank, $\sim 59.2\%$ that of salol, and $\sim 63.1\%$ that of the hydroxy phenyl derivative of benzophenone UV absorber. The results of the percent gelation of photodegraded PVC blank and for PVC stabilized with either of the investigated stabilizers are represented in Table II and Figure 2. The results of the percent gelation of photodegraded PVC in the presence of the two reference stabilizers are also given for comparison. The results clearly reveal the lower extent of gelation of all the investigated phenyl urea derivatives when compared with the blank and the two reference stabilizers, and the order of magnitude in the lower extent of gelation in case of the investigated stabilizers is highly remarkable till the end of the exposure time (Table II). However, the rate of gelation for irradiated PVC films in presence of the

investigated stabilizers does not coincide with the rate of weight loss for the same investigated samples, especially at the early stages of photodegradation (3 h). This is in contrast to the results obtained in case of the blank or those films stabilized by the commercially known UV stabilizers (taking as references). This experimental finding is most probably attributed to the different mechanisms by which the organic stabilizers work when compared with the UV absorbers.

The organic stabilizer interferes with the degradative products (free-radicals) resulting from the photodegradation of the polymer; thus, at the early stages of degradation (stabilizer concentration is high), the organic stabilizers trap the free radicals and at the same time block the radical sites created on the PVC chains, thus minimizing the evolution of HCl gas and consequently lower the weight loss (%). But this most probably happened at the expense of the formation of few crosslinks which are formed in the absence of the organic stabilizers (i.e., in case of PVC blank or PVC stabilized with UV absorbers). At the subsequent stages of degradation (6 h and more), most of the photostabilizers are already incorporated in the polymeric matrix and are exhausted as radical trappers.

For this, the rate of weight loss and the rate of gelation at the subsequent stages of degradation are more close than those at the early stages of degradation.

Moreover, the data obtained for the percentage of soluble fraction for photodegraded blank PVC, or for photodegraded PVC in presence of reference stabilizers or in presence of the investigated phenyl urea derivatives as a function of irradiation time agree well with the data obtained for the percent gelation (Table II and Fig. 3), which gives an additional proof for the results obtained for the amount of gel formation.

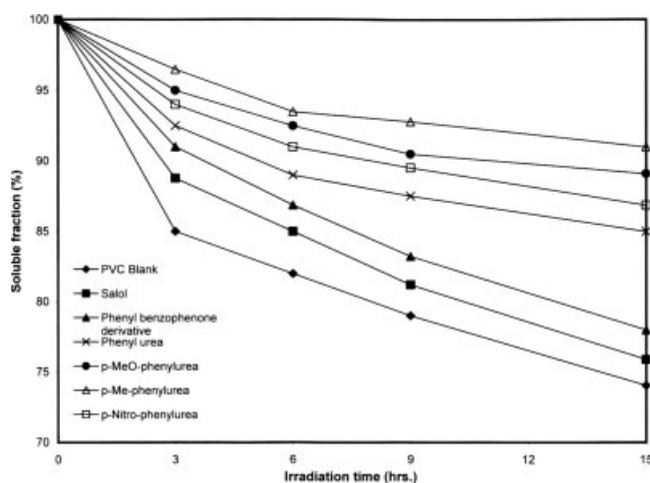


Figure 3 Variation of soluble fraction (%) of phenyl urea derivatives with irradiation time (h).

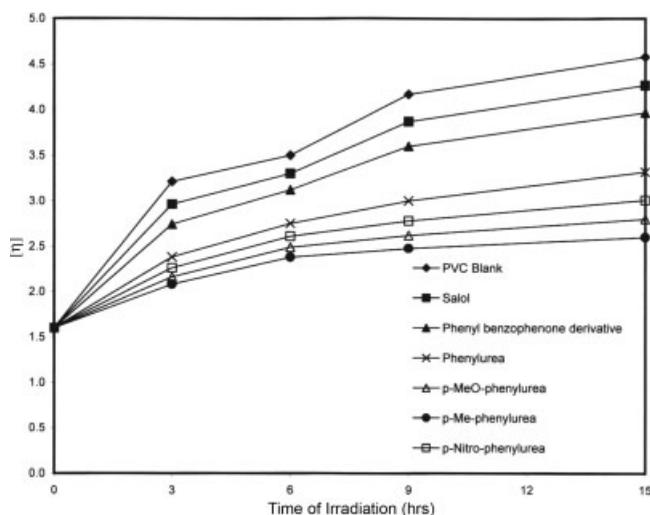


Figure 4 Variation of intrinsic viscosity for phenyl urea derivatives with irradiation time (h).

Intrinsic viscosity measurements as criterion for photo-stabilizing efficiency

An additional proof for the potency of phenyl urea derivatives to intervene with the free radical chain degradation mechanism of rigid PVC during photo-irradiation comes from the relatively lower viscosities of the soluble fractions of the degraded polymer in the presence of the investigated organic stabilizers when compared with those of either the nonradiated blank or PVC samples stabilized with the two reference UV stabilizers (Table II and Fig. 4).

These results can be taken as evidence that phenyl urea stabilizers protect the degraded polymeric chains at least partially through blocking the odd electron sites created on the PVC chains during photodegradation and consequently minimize the possibility for the recombination of macroradicals.

Mechanisms for the stabilizing mode of action of phenyl urea derivatives based on the aforementioned explanation imply that the ability of these compounds to be incorporated into the body of the polymeric chain is to be expected and factors favoring this ability will accordingly lead to better efficiencies.

This has been experimentally proved based on the following observations:

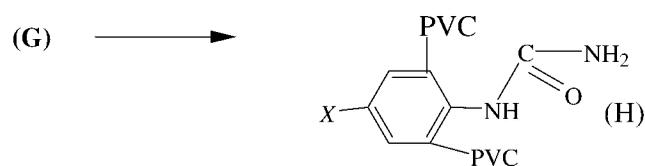
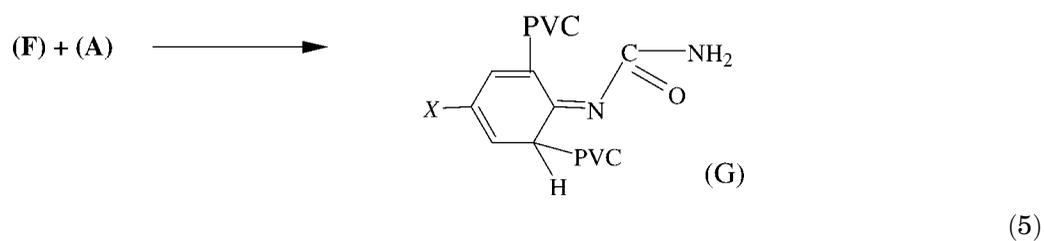
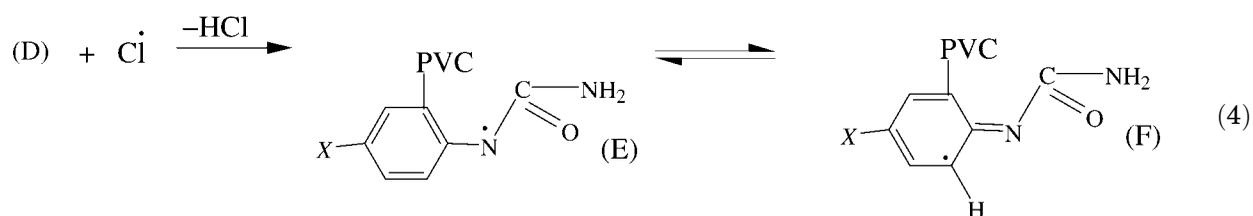
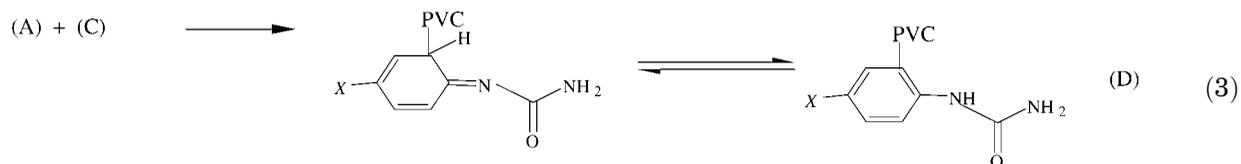
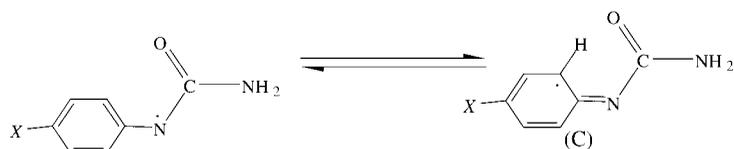
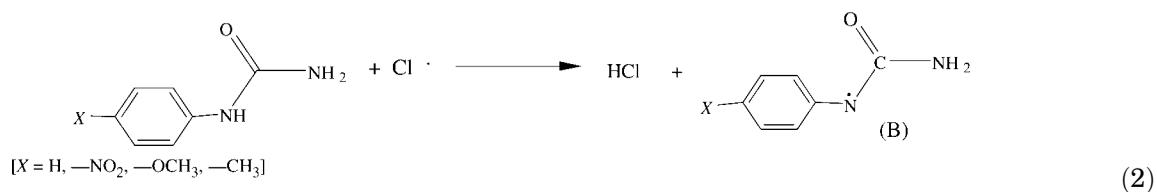
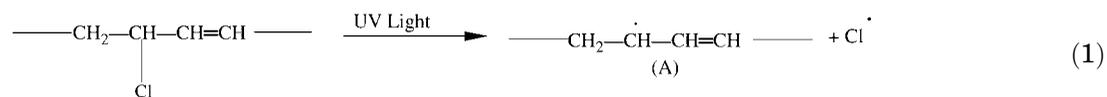
1. When the organic stabilizer ($p\text{-CH}_3\text{-}\Phi$ urea: p -tolyl urea) alone was subjected to a stream of HCl gas, under UV lamp for 30 min, the elemental analysis showed the absence of Cl (Nil %), which indicates that the mentioned derivative cannot interact with the evolved HCl gas.
2. Elemental analysis of PVC photodegraded films in presence of $p\text{-CH}_3\text{-}\Phi$ urea—after extensive wash with hot ethanol to get rid of unreacted stabilizer—indicated the presence of N (0.37%) at 9 h of irradiation and N (0.5%) at 15 h. IR spectrum of PVC in the presence of $p\text{-CH}_3\text{-}\Phi$ urea (3 h) showed a new band at 1647 cm^{-1} specific for the linkage —C=N [eq. (3)], whereas the IR spectrum of $p\text{-CH}_3\text{-}\Phi$ urea (6 and 9 h) showed a band at 1593 cm^{-1} specific for amine salt formation [eq. (6)], which implies the incorporation of the stabilizers moiety in the body of the polymeric chain.
3. To examine the efficiency of $p\text{-CH}_3\text{-}\Phi$ urea—taken as example—as a radical trap, the organic stabilizers were dissolved in CCl_4 and the solution was subjected to a low-pressure UV lamp for 120 min. Benzophenone was added—in a catalytic amount—to enhance the radical decomposition of CCl_4 . The elemental analysis proved the presence of chlorine in the irradiated sample ($\text{Cl}\% = 1.5\%$). IR spectrum of the irradiated stabilizer showed a new band at 6323 cm^{-1} specific for C—Cl bond.
4. Another experimental proof for the high stabilizing efficiency of the investigated stabilizers, when compared with the reference stabilizers, is shown from the lower rate of discoloration of samples stabilized with $p\text{-CH}_3\text{-}\Phi$ urea—taken as examples—relative to the blank sample and PVC samples stabilized with any of the reference stabilizers (Table III).

From the above-mentioned experimental findings, one can suggest a probable radical mechanism for the stabilizing efficiency of the investigated stabilizers during the photodegradation of PVC:

TABLE III
Extent of Discoloration of Photo-Degraded Films of Rigid PVC, in the Presence of 2 wt % of the Investigated Stabilizers as a Function of Irradiation Time

Type of stabilizer	Irradiation time (h)				
	0	3	6	9	15
PVC blank	White	Pale brown	Pale brown	Pale brown	Pale brown
PVC + A	White	Light yellow	Light yellow	Light yellow	Dark yellow
PVC + B	White	Light yellow	Light yellow	Light yellow	Light brown
PVC + $p\text{-CH}_3\text{-}\Phi\text{U}$	White	White	White	White	Yellow

A indicates phenyl salicylate (Salol); B, methanone, 2-hydroxy-4-(octyloxy)-phenylbenzophenone.



*In the later stages of degradation:

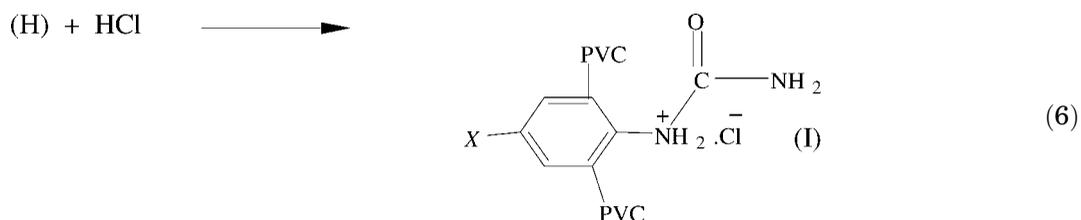




Figure 5 PVC blank film (nonirradiated).

According to the proposed mechanism, the labile chlorine atom is detached from the PVC chain and abstracts a H atom of the NH— of the amide linkage in urea derivative, leaving an odd electron on the N-atom which delocalizes on the phenyl ring to recombine with the odd electron on the PVC chain. This step is repeated again to add another PVC chain in the other O-position to the NH— group [eq. (5)]. In the later stages, the stabilizer forms an amine salt. This mechanism is evidenced by the IR spectra for PVC in the presence of *p*-CH₃-Φ urea (irradiated for 3 h) as a band at 1647 cm⁻¹ appeared characteristic for —C=N stretching vibrations [eq. (4)], while for PVC in presence of *p*-CH₃-Φ urea (irradiated for 6 and 9 h), one band appeared at 1674 cm⁻¹

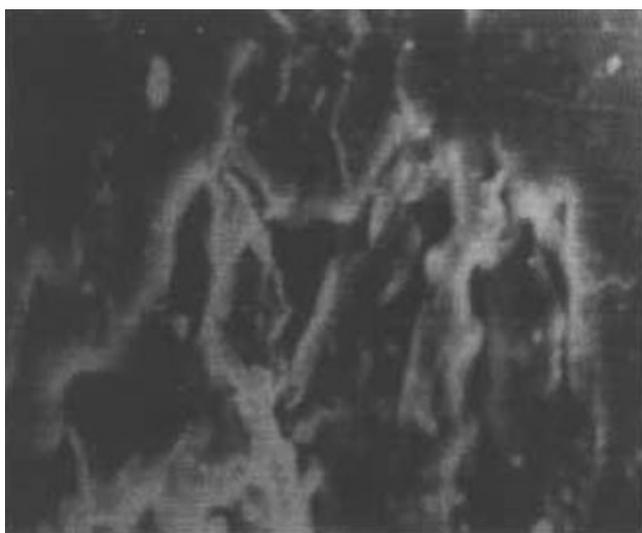


Figure 6 PVC film (irradiated for 15 h).

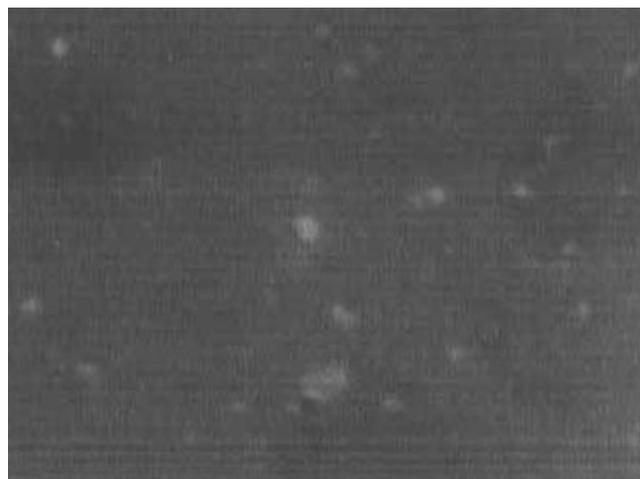


Figure 7 *p*-Tolyl film (irradiated for 15 h).

characteristic for the amide carbonyl stretching vibrations [eqs. (4) and (5)]. Moreover, two bands appeared at 1520 and 1593 cm⁻¹ characteristic for the N—H bending for amine salt at the later stages of degradation [eq. (6)].

It was found that when the *p*-substituent in the phenyl ring of urea was of the electron donor type, it increases the electron density on the O- and P-positions which facilitates the mechanism to proceed and also the results of weight loss (%) and gel content (%) of these derivatives are much better than those of the nonsubstituted derivatives and the electron-withdrawing substituted derivatives.

Surface morphology by using SEM (magnification, 200x) as criterion for photo-stabilizing efficiency

p-CH₃-Φ urea (*p*-tolyl urea) derivative is taken as a representative example for the phenyl urea derivatives to examine its surface morphology after (15 h) irradiation because it gives the least gel content (%) at 15 h than any of the other derivatives.

The surface morphology of films of PVC (nonirradiated) (Fig. 5), PVC (irradiated for 15 h) (Fig. 6), and PVC in presence of *p*-CH₃-Φ urea (irradiated for 15 h.) (Fig. 7) were studied using SEM. PVC (nonirradiated) film surface is smooth and void of any white spots, indicating photodegradation, whereas PVC (irradiated for 15 h) film surface is full of white spots, indicating the holes or groves where HCl evolves after photoirradiation. In PVC in the presence of *p*-CH₃-Φ urea (irradiated for 15 h.), the surface is almost smooth and less white spots appear, indicating the great stabilizing efficiency of the stabilizer and how much the stabilizer protects the polymer surface from deterioration via dehydrochlorination process.

TABLE IV
Weight Loss, Soluble Fraction, Gel Content, and Intrinsic Viscosity
for the Blends of the Investigated Material with Different Ratios
of Photo-Stabilizers Radiated for 9 h

Stabilizer type	Weight loss (%)	Gel content (%)	Soluble fraction (%)	Intrinsic viscosity [η] (dL/g)
A (100%)	4.81	18.89	81.2	3.87
<i>p</i> -CH ₃ - Φ U (25%) : A (75%)	2.54	7.32	92.4	2.13
<i>p</i> -CH ₃ - Φ U (50%) : A (50%)	2.26	6.87	93	1.98
<i>p</i> -CH ₃ - Φ U (75%) : A (25%)	1.98	6	94	1.76
<i>p</i> -CH ₃ - Φ U (100%)	2.83	7.73	92.77	2.477
B (100%)	4.38	16.43	83.22	3.6
<i>p</i> -CH ₃ - Φ U (25%) : B (75%)	2.53	7.32	92.68	2
<i>p</i> -CH ₃ - Φ U (50%) : B (50%)	2.05	6.35	93.5	1.85
<i>p</i> -CH ₃ - Φ U (75%) : B (25%)	1.83	5.87	94.12	1.72
<i>p</i> -CH ₃ - Φ U (100%)	2.83	7.73	92.77	2.477

A indicates phenyl salicylate (Salol); B, methanone, 2-hydroxy-4-(octyloxy)-phenyl-benzophenone. PVC (nonradiated) [η] = 1.6.

Effect of mixed stabilizers on the stabilization efficiency of photo-degraded rigid PVC

The study is extended to investigate the effect of mixing the *p*-CH₃- Φ urea (*p*-tolyl urea) derivative—taken as a representative example for phenyl urea derivatives—with the two reference photostabilizers on the stabilization efficiency of degraded rigid PVC. Because of the efficiency of *p*-CH₃- Φ urea as a radical trapper for radical species that might result from photoirradiation and as phenyl salicylate and hydroxy-phenyl benzophenone derivative act as UV absorbers, blending of the investigated stabilizer with both reference stabilizers most probably lead to a combination between their mechanisms of action. Mixing was done in the ranges of 0–100% of the

investigated stabilizers relative to either of the reference stabilizers used. The overall mixed stabilizers concentration was taken as 2 g/100 g PVC and the results represent the average of three comparable experiments for each stabilizer mixture. Results of weight loss percent, gel content percent, soluble fraction percent, and intrinsic viscosity for each combination irradiated for 9 h are illustrated in Table IV and Figures 8 and 9. The results reveal the existence of a true synergistic effect resulting from the combination of the organic stabilizer (*p*-CH₃- Φ urea) with any of the two reference stabilizers. The maximum synergism was achieved when *p*-CH₃- Φ urea stabilizer was mixed with both reference stabilizers in a weight ratio of 75 : 25%. The results also reveal the

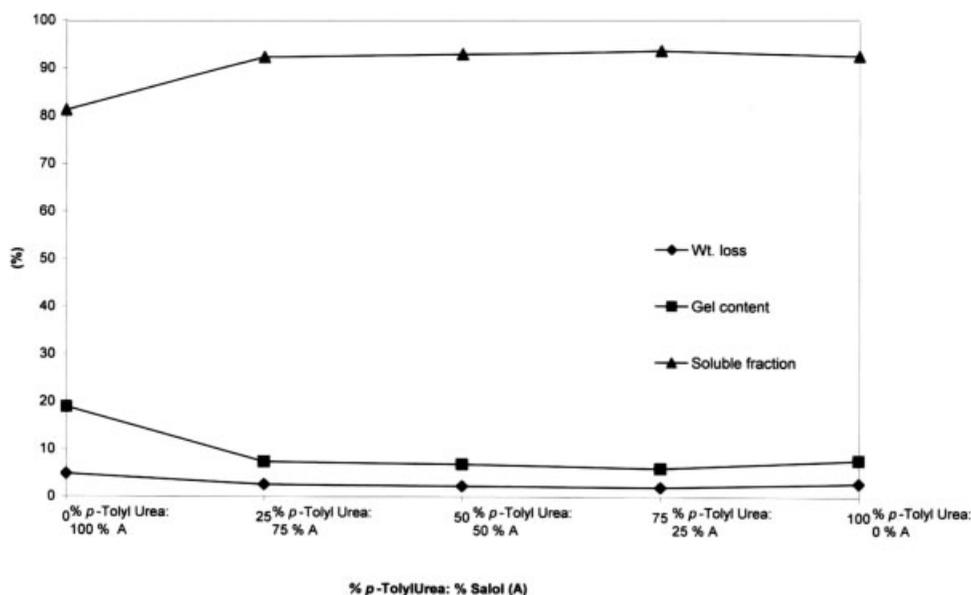


Figure 8 Variation of weight loss (%), gel content (%), and soluble fraction (%) for PVC in presence of mixed stabilizer (*p*-tolyl urea% : Salol (A) %) irradiated for 9 h.

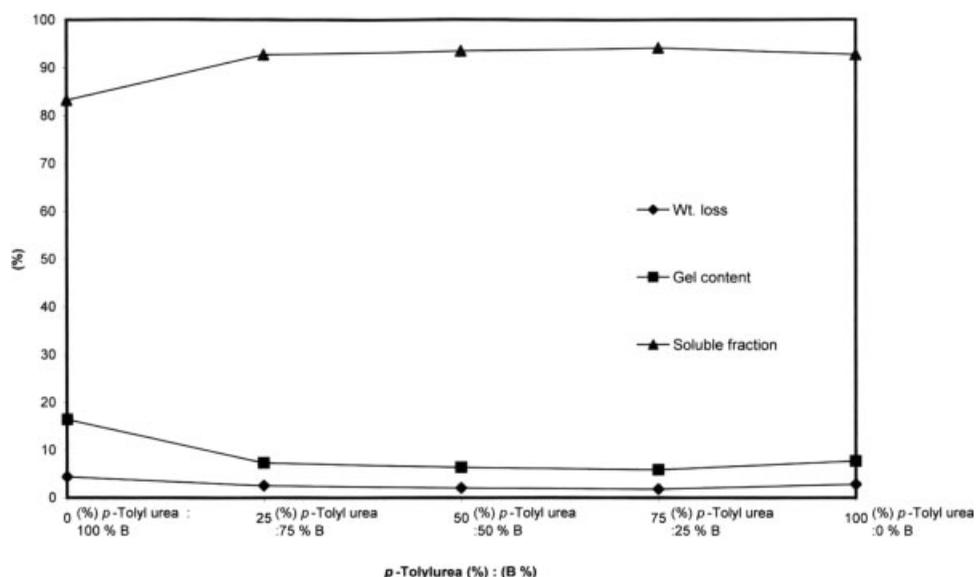


Figure 9 Variation of weight loss (%), gel content (%), and soluble fraction (%) of PVC in presence of mixed stabilizer (*p*-tolyl urea % : phenyl benzophenone derivative (B) %) irradiated for 9 h.

TABLE V
Extent of Discoloration of Photo-Degraded Films of Rigid PVC, for 9 h, in Presence of Some Representative Examples of Mixed Photo-Stabilizers

Yellow A (100%) : <i>p</i> -CH ₃ -ΦU (0%)	White A (75%) : <i>p</i> -CH ₃ -ΦU (25%)	White A (50%) : <i>p</i> -CH ₃ -ΦU (50%)	White A (25%) : <i>p</i> -CH ₃ -ΦU (75%)	White A (0%) : <i>p</i> -CH ₃ -ΦU (100%)
Yellow B (100%) : <i>p</i> -CH ₃ -ΦU (0%)	Yellow B (75%) : <i>p</i> -CH ₃ -ΦU (25%)	White B (50%) : <i>p</i> -CH ₃ -ΦU (50%)	White B (25%) : <i>p</i> -CH ₃ -ΦU (75%)	White B (0%) : <i>p</i> -CH ₃ -ΦU (100%)

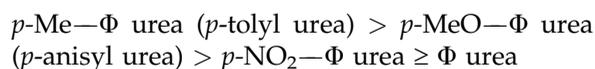
A indicates phenyl salicylate (Salol); B, methanone, 2-hydroxy-4-(octyloxy)-phenyl-benzophenone.

improvement in the extent of discoloration as shown in Table V when *p*-CH₃-Φ urea stabilizer was mixed with both reference stabilizers, especially in a weight ratio of (75 : 25%).

CONCLUSIONS

These can be summarized as follows:

1. Phenyl urea derivatives have been investigated as efficient photostabilizers for rigid PVC. This stabilizing efficiency of the investigated photostabilizers was found to follow the following order:



The stabilizing efficiency of these derivatives is attributed to their radical trapping potency which intervenes with the radical degradation process of PVC. This was also achieved by blocking the odd electron sites on the polymeric chains.

2. *p*-CH₃-Φ urea exhibits greater efficiency when used in combination with both of the UV absorbers. The results of the blending with the reference stabilizers decreases both the weight loss and the extent of crosslinking of the polymer compared with that in presence of either UV absorbers or the investigated stabilizers.
3. Moreover, the observed synergistic effect is attributed to the combination of the mechanisms by which both *p*-CH₃-Φ urea and reference stabilizers work. Maximum synergism is obtained at the weight ratio, investigated stabilizers : reference stabilizer = 75 : 25%.

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