

Thermal Degradation Behavior of Poly(vinyl chloride) in Presence of Poly(*N*-acryloyl-*N'*-cyanoacetohydrazide)

Nadia A. Mohamed,¹ Zeinab R. Farag,² Magdy W. Sabaa¹

¹Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

²Department of Chemistry, Faculty of Science, El-Fayoum University, El-Fayoum, Egypt

Received 13 May 2007; accepted 29 July 2007

DOI 10.1002/app.27530

Published online 7 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal degradation behavior of poly(vinyl chloride), PVC, in presence of poly(*N*-acryloyl-*N'*-cyanoacetohydrazide), PACAH, has been studied using continuous potentiometric determination of the evolved HCl gas from the degradation process from one hand and by measuring the extent of discoloration of the degraded samples from the other. The efficiency of blending PACAH with dibasic lead carbonate, DBLC, conventional thermal

stabilizer has also been investigated. A probable radical mechanism for the effect of PACAH on the thermal stabilization of PVC has been proposed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2362–2368, 2008

Key words: poly(vinyl chloride); poly(*N*-acryloyl-*N'*-cyanoacetohydrazide); thermal dehydrochlorination; discoloration; stabilization mechanism; costabilizer

INTRODUCTION

Poly(vinyl chloride), PVC, is an intrinsically thermally unstable polymer. It undergoes an extensive degradation especially during its molding and applications at high temperatures, which can reduce the useful life of the articles. Its thermal degradation occurs by autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds.¹ This results in an unacceptable discoloration of the polymer and lack of its physical and mechanical properties.² The sensitivity of the polymer towards thermal treatment has been attributed to the greater reactivity of the labile sites in the polymer chains. The degradation mechanism involves two basic steps namely initiation through labile structures and propagation or the build up to polyenes. Initiation often occurs due to the presence of a few abnormal structures such as allylic chlorine,³ tertiary hydrogen and chlorine atoms,⁴ terminal end groups such as double bonds,⁵ oxygen containing groups,⁶ or peroxide residues,⁷ head-to-head structures,⁸ and steric order of the monomer (tacticity).⁹ In general, the great commercial importance of PVC can be attributed to the development of effective means of stabilization. The thermal stabilizers commonly in use for the stabilization of PVC are either basic salts¹⁰ which can react with the evolved hydrogen

chloride gas, thus retarding the deleterious catalytic action of the eliminated hydrogen chloride,¹¹ metallic soaps,¹² and esters or mercaptides of dialkyltin¹³ that can exchange the labile chlorine in the backbone chains by other more stable ester or mercaptide groups derived from the stabilizer. Moreover, quinone-tin polymers have been used as thermal stabilizers through intervention with the radical degradation products.¹⁴ Stabilizers of an organic nature have recently been established for the thermal stabilization of PVC.^{15–18} Blending of PVC with another polymer as the second component was also used for the improvement of its heat stability. The second polymers included either addition polymers such as poly(methyl methacrylate),¹⁹ poly(styrene),²⁰ poly(vinyl butyral),²¹ and cis-polybutadiene²² or step-growth polymers like poly(tetramethylene sebacate),²³ poly(dimethylsiloxane),²⁴ bisphenol A polycarbonate,²⁵ and poly(ethylene adipate).²⁶

N-acryloyl-*N'*-cyanoacetohydrazide (ACAH) and its metal complexes have proved to be effective additives for stabilization of PVC against thermal degradation.¹⁵ ACAH possesses in its structure a wide variety of reactive functional groups in addition to a highly conjugated system. This unique structure provides the compound with the ability to intervene in the degradation process as a powerful radical trap. In view of some structural similarity of poly(*N*-acryloyl-*N'*-cyanoacetohydrazide), PACAH, to ACAH, the objective of this research work is to study the thermal characteristics of PVC in presence of PACAH. Our attention has been confined to a low composition range from 0 to 5% PACAH based on

Correspondence to: M. W. Sabaa (magdysabaa@hotmail.com).

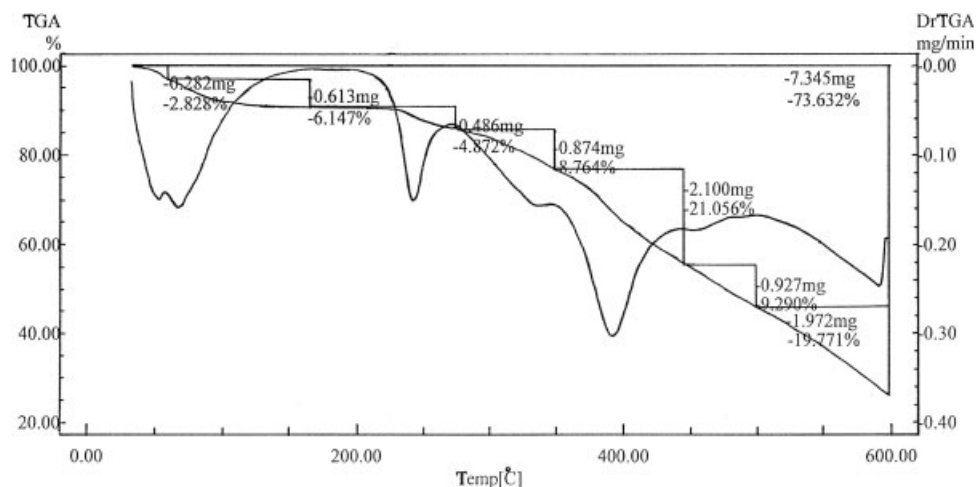


Figure 1 Thermogravimetric analysis (TG) of PACAH in air atmosphere.

the weight of PVC to keep the other characteristics of PVC unchanged.

EXPERIMENTAL

Materials

Poly(vinyl chloride), PVC, suspension, from Hüls Company (Germany) with *K* value of 70, dibasic lead carbonate (DBLC) from the National Lead Company (Germany) were used for this investigation. Benzophenone was obtained from Sigma-Aldrich Germany and Carbon tetrachloride was obtained from El-Nasr Company for Medicinal Chemicals, Cairo-Egypt.

PACAH,²⁷ was prepared by dissolving acryloyl cyanoacetohydrazide (1 mol) and both sodium bisulfite and potassium persulfate (10^{-2} mol) in 1 L of secondary distilled water. The resulting solution was then polymerized in a water bath at 55–60°C for 3 h. The precipitated PACAH was then filtered, washed thoroughly with secondary distilled water and dried.

The prepared PACAH is thermally stable till 200°C as indicated from its thermogravimetric analysis (TG), Figure 1; (Shimadzu TGA-50H, the thermal analysis was performed in air at a flow rate of 20 mL/min and a heating rate of 10°C/min) Its intrinsic viscosity is 3.67 cm³/g, in DMF at 25°C. The polymer concentration was 0.01 g/cm³.

Preparation of PVC samples

PVC rigid samples were prepared according to the following recipe:

PVC	1 g
DBLC	2 wt %
PACAH	0–5 wt %

The mixture is thoroughly mixed in a mortar, and 0.2 g of the resulting fine powder was used for each

experiment. The results obtained are the average of three experiments for each test.

Methods of evaluation of the stabilizing efficiency

Evaluation of the stabilizing efficiency was carried out by measuring the dehydrochlorination rate using a continuous potentiometric determination of the evolved hydrogen chloride. A detailed description of this method is given elsewhere.²⁸ A digital pH-meter (potentiometer) of the type CG 822 (Schott Grade GmbH, Germany) was used. It was connected to a silver electrode and a saturated calomel reference electrode for the potentiometric measurements. The extent of discoloration of the degraded PVC samples was evaluated visually as a function of degradation time.

IR spectra were recorded using a Tescan Shimadzu Infrared Spectrophotometer (FTIR 8000, Japan) in the wave number range from 4000 to 400 cm⁻¹ at 25°C. Elemental analyses were performed at the Micro analytical unit, Cairo University.

RESULTS AND DISCUSSION

Results of the dehydrochlorination rates of rigid PVC thermally degraded at 180°C, in air, in presence of various concentrations of the polymeric additive PACAH blended with 2 wt % of DBLC commercial thermal stabilizer are shown in Figure 2. Results of a nonstabilized blank sample and that of the sample stabilized with 2 wt % of DBLC are also given for comparison.

The results as shown from Figure 2 clearly reveal the remarkable improvement in the stabilizing efficiency of PVC stabilized by DBLC in presence of the investigated polymeric stabilizer (PACAH), and this improvement increases as a function of increasing the concentration of PACAH in the PVC

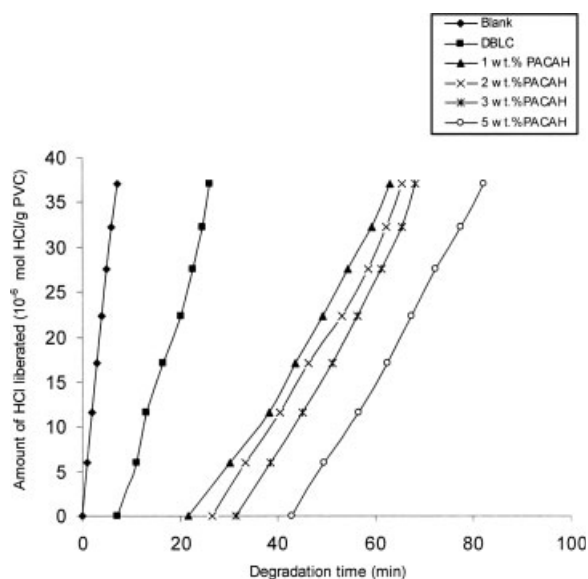


Figure 2 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in presence of 2 wt % DBLC commercial stabilizer blended with various concentrations of PACAH.

samples. This remarkable improvement is illustrated not only by the presence of a well defined thermal stability value (T_S), during which no detectable amounts of hydrogen chloride gas are liberated, but also by the lower rates of dehydrochlorination during the subsequent stages of the degradation reaction (Figure 2).

Figure 3, on the other hand, represents the rate of dehydrochlorination of PVC samples stabilized with various concentrations of PACAH used alone as thermal stabilizers (i.e., in absence of DBLC) as compared with the nonstabilized blank sample and that stabilized with 2 wt % DBLC. The results clearly reveal the improvement of both the T_S values and the rates of dehydrochlorination as a function of the increase of PACAH concentration. Moreover, the results also demonstrate the slower rate of dehydrochlorination of PVC sample stabilized with 2 wt % of PACAH as compared with that stabilized with the same concentration of DBLC. However, both of these two samples showed an identical T_S value (7 min).

The effect of adding PACAH in various concentrations to PVC samples in presence and in absence of DBLC on the extent of discoloration of polymer at various time intervals (before and after the T_S values) is illustrated in Tables I and II, respectively. The results clearly show the low extent of discoloration of PVC samples stabilized with PACAH either in presence or absence of 2 wt % DBLC as compared with the blank samples. However, PVC sample stabilized with 2 wt % DBLC reference stabilizer showed lower extent of discoloration as compared with PVC samples stabilized by PACAH either in presence or

absence of the reference stabilizer, and the samples stabilized by the polymeric stabilizer alone (i.e., in absence of DBLC, Table II) showed lower extent of discoloration relative to those in presence of 2 wt % DBLC (Table I), irrespective of the polymeric stabilizer concentration.

To suggest a probable mechanism for the stabilizing action of PACAH, the following experiments were performed:

1. A stream of hydrogen chloride gas was allowed to pass in the degradation tube over a sample of PACAH heated at 180°C, in air, for 30 min. The IR spectrum of the obtained product showed the disappearance of the =NH stretching band at 3600–3100 cm^{-1} , together with a remarkable lowering in the peak intensities at 2260 and 1670 cm^{-1} corresponding to $-\text{C}\equiv\text{N}$ and $=\text{C}=\text{O}$ groups, respectively (Fig. 4). Moreover, the IR spectrum showed the appearance of C–Cl and $-\text{CO}-\text{Cl}$ stretching band at 763 and 1760 cm^{-1} , respectively, in addition to the detection of chlorine in the polymeric stabilizer (element test). This indicates that PACAH has the ability to interact with the evolved HCl gas.
2. Another experiment was performed to examine the efficiency of PACAH as a radical trap. The polymer was suspended in carbon tetrachloride (a solvent which gives chlorine atoms on photolysis) and the solution was subjected to a low pressure mercury lamp for 120 min. Benzophenone in

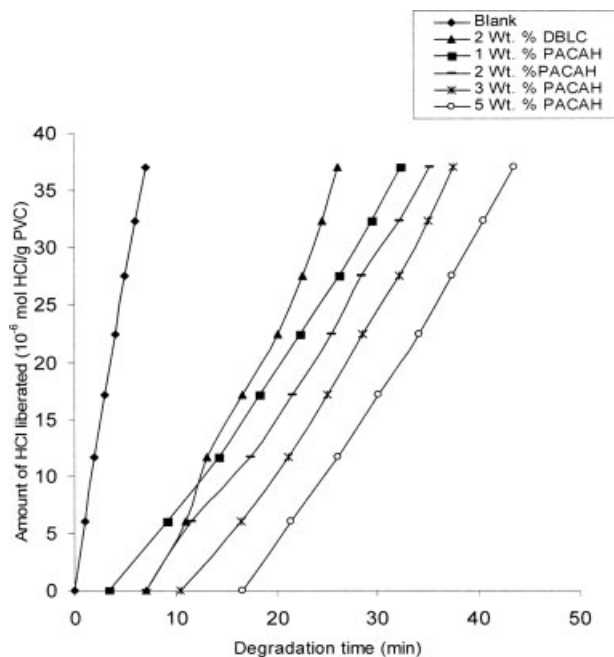


Figure 3 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in presence of various concentrations of PACAH.

TABLE I
Extent of Discoloration of Thermally Degraded Rigid PVC at 180°C, in Air, in Presence of 2 wt % DBLC Blended with Various Concentrations of PACAH as a Function of Degradation Time

Stabilizer(s) concentration	Discoloration thermal degradation time (min)				
	0	10	20	30	45
Blank	Colorless	Brown	Dark brown	Dark brown	Dark brown
2 wt % DBLC	Colorless	Buff	Buff	Orange	Orange
1 wt % PACAH	Colorless	Buff	Pale brown	Brown	Brown
2 wt % PACAH	Colorless	Pale brown	Brown	Brown	Brown
3 wt % PACAH	Colorless	Pale brown	Brown	Brown	Brown
5 wt % PACAH	Colorless	Pale brown	Brown	Brown	Dark brown

a catalytic amount was added to enhance the radical decomposition of CCl_4 . The elemental analysis has proved the presence of chlorine in the irradiated solid sample, and consequently, this result indicates that PACAH can act as a radical trap.

- A third series of experiments has been made by following the IR spectrum of PVC samples in presence of the polymeric additive subjected to thermal degradation at 180°C, in air, for different time intervals (from 10 to 60 min). In these experiments, PACAH was used in a higher concentration (5 wt %) to facilitate the detection of any changes in the measured spectra, and the degraded samples were subjected to extensive washing with boiled secondary distilled water to remove any residual unreacted PACAH (Fig. 5). The results show the appearance of a new band at 2264 cm^{-1} which corresponds to the $-\text{C}\equiv\text{N}$ group of the polymeric additive. This in addition to a new band at 1674 cm^{-1} which corresponds to $-\text{CO}-\text{NH}-$ linkage and that this peak is lowered in intensity with the time of degradation. These results indicate that the PACAH is attached chemically to the PVC chains through its nitrile group. This is probably followed by a cleavage of the imide linkage at the later stages of the stabilization. Moreover, the newly band formed near 1500 cm^{-1} which correspond to the formation of quater-

nary ammonium salt and which appears at the later stages of stabilization gives an additional proof for the possibility of this polymeric stabilizer to act as an HCl absorber.

- The elemental analysis of the degraded PVC residue, in presence of various concentrations of PACAH, before and after the induction period, and after the extensive washing with boiled distilled water to get rid of any residual PACAH, has shown that nitrogen is present in the degraded PVC samples. This indicates that PACAH molecule or at least a part of it is chemically bonded to the PVC matrix.

From the aforementioned experiments, a probable free-radical mechanism of stabilization which could account for all the experimental findings, may be represented as follows:

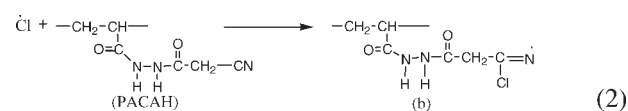
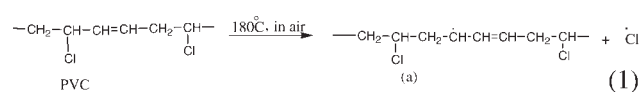


TABLE II
Extent of Discoloration of Thermally Degraded Rigid PVC at 180°C, in Air, in Presence of Various Concentrations of PACAH as a Function of Degradation Time

Stabilizer(s) concentration	Discoloration thermal degradation time (min)				
	0	10	20	30	45
Blank	Colorless	Brown	Dark brown	Dark brown	Dark brown
2 wt % DBLC	Colorless	Buff	Buff	Orange	Orange
1 wt % PACAH	Colorless	Buff	Pale brown	Brown	Brown
2 wt % PACAH	Colorless	Buff	Brown	Brown	Brown
3 wt % PACAH	Colorless	Buff	Brown	Brown	Brown
5 wt % PACAH	Colorless	Buff	Brown	Brown	Brown

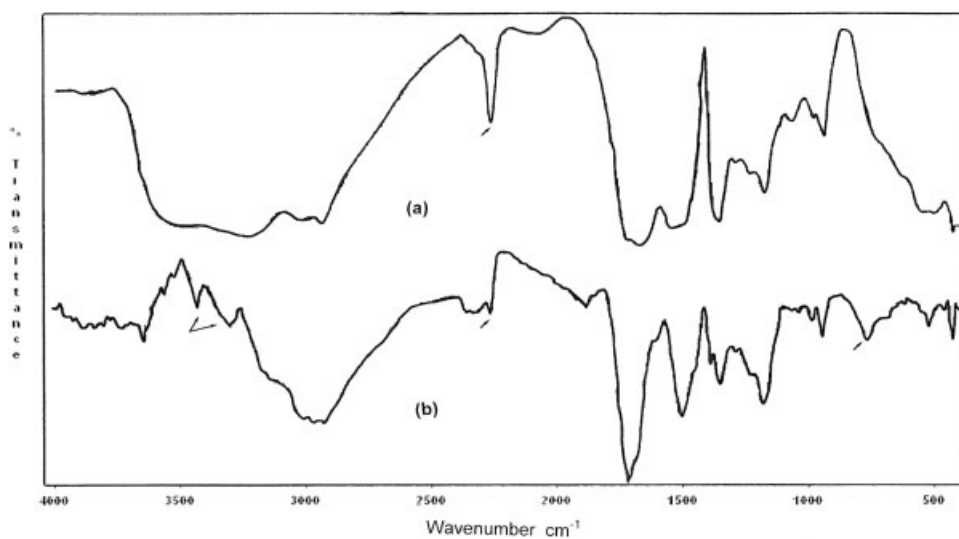


Figure 4 IR spectra of PACAH: (a) before treatment; (b) after treatment with HCl gas at 180°C for 30 min.

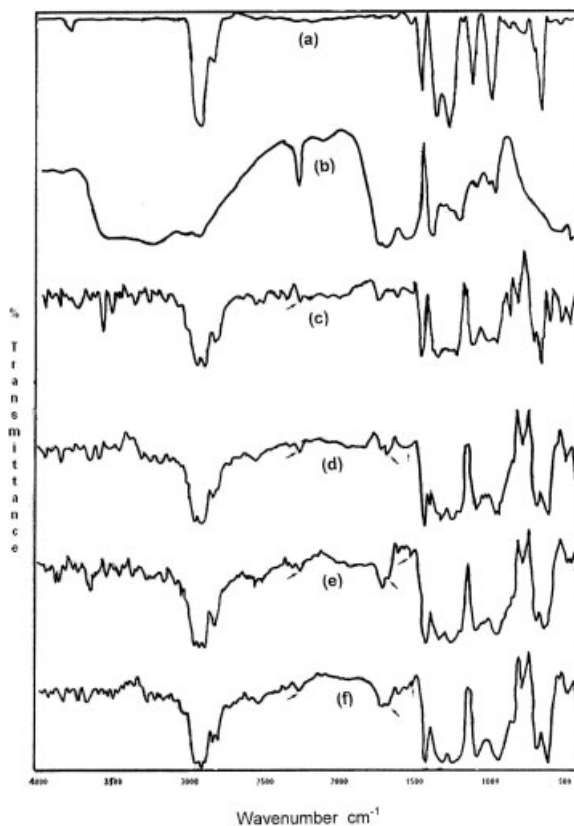
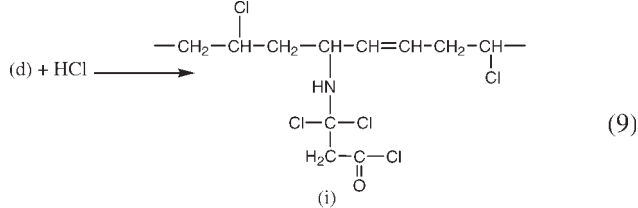
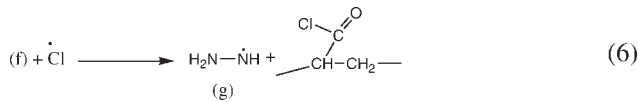
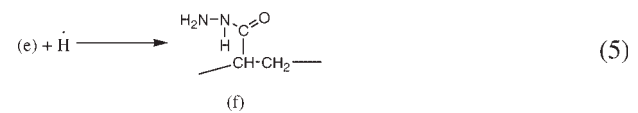
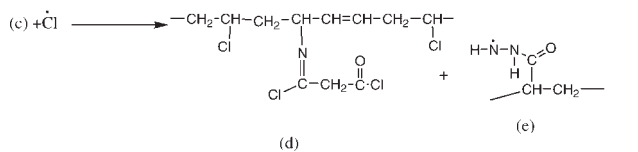
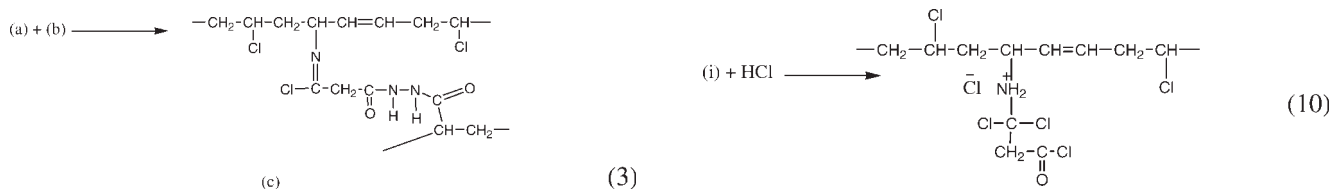


Figure 5 Change in the IR spectra of PVC samples degraded at 180°C, in air, in the presence of PACAH as a function of degradation time: (a) virgin PVC; (b) PACAH; (c) 10 min; (d) 20 min; (e) 40 min; (f) 60 min.

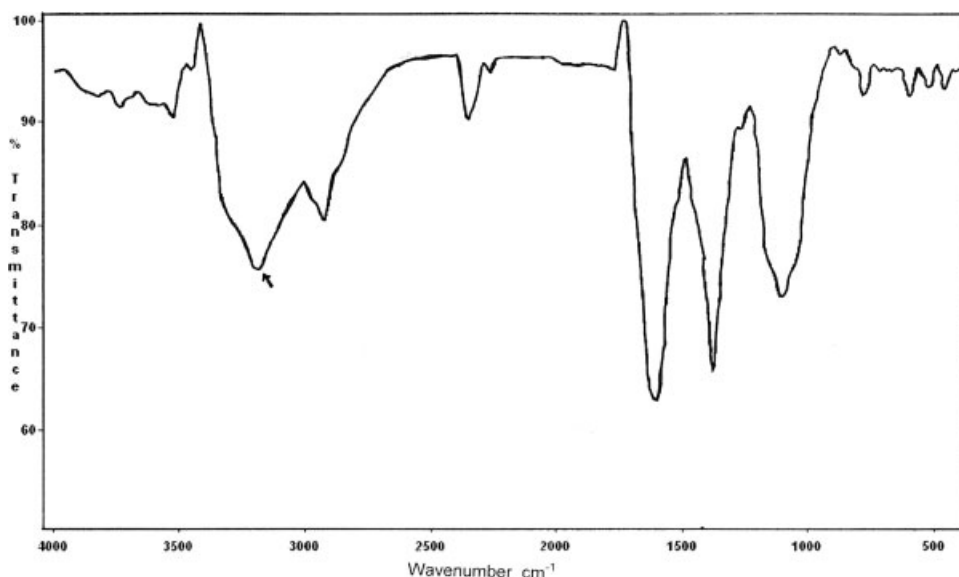


Figure 6 IR spectra of residual PACAH extracted from the degraded PVC for 30 min at 180°C, in air.

According to the suggested mechanism, the labile chlorine atom detached from the PVC molecule eq. (1) is trapped by the PACAH molecule through its nitrile group resulting in the formation of PACAH radical eq. (2). Once formed, the PACAH radical block the radical site on the PVC chain, thus disrupting the radical chain degradation of PVC eq. (3). On the other hand, the lower in the intensity of the amide linkage (IR peak at 1670 cm^{-1}) as a function of degradation time is in good accordance with the subsequent steps of the proposed stabilization mechanism in which the chlorine atoms detached from

the PVC molecules attack the imide linkages eqs. (4)–(6). The IR spectrum of the residual PACAH left behind the washed degraded PVC sample after 30 min degradation showed strong peak near 3180 cm^{-1} which correspond to the amine salt (hydrazine hydrochloride), (Fig. 6), this supports eq. (4) of the proposed mechanism and the subsequent steps. Moreover, eqs. (8)–(10) represent another possibility of stabilization at the latter stages of degradation (i.e., after the T_s) through the absorption of the evolved HCl gas.

This interpretation seems to be reasonable for two reasons:

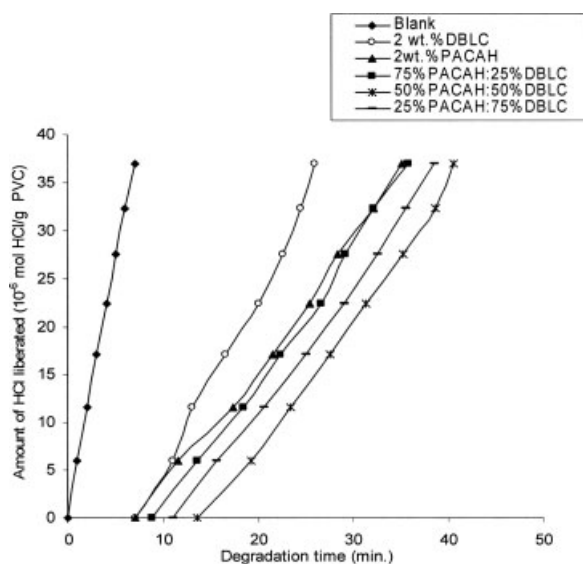


Figure 7 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in presence of various weight ratios of PACAH mixed with DBLC. The overall mixed stabilizers concentration was kept constant at 2% based on the weight of PVC.

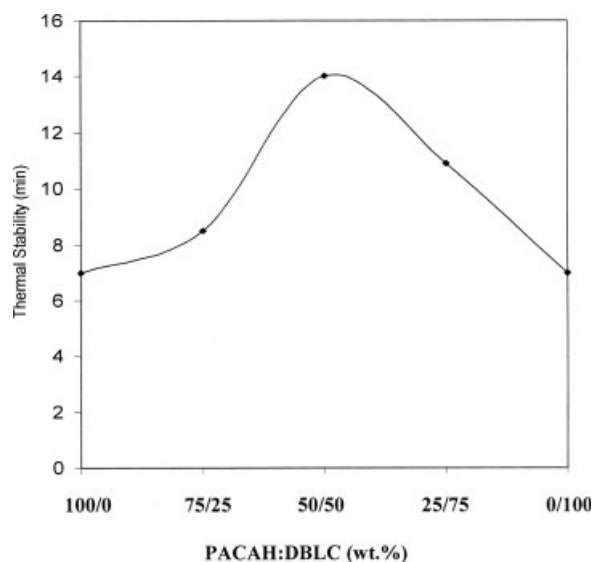


Figure 8 Thermal stability (T_s) composition curve for PACAH and DBLC mixtures.

TABLE III
Extent of Discoloration of Thermally Degraded Rigid PVC at 180°C, in Air, for 30 min in Presence of Various Weight Ratios of PACAH Mixed with DBLC

PACAH/DBLC weight ratio	Discoloration
0/0	Dark brown
0/100	Orange
25/75	Orange
50/50	Pale orange
75/25	Orange
100/0	Brown

The overall mixed stabilizers concentration was kept constant at 2% based on the weight of PVC.

1. The true synergistic effect observed when the investigated polymeric stabilizer is added to DBLC commercial stabilizer. This synergistic effect is due to the different mechanisms by which the two stabilizers work. The former acts as a radical trap while the latter as HCl absorber.
2. The high extent of discoloration of PVC samples stabilized by the polymeric stabilizer at the later stages of degradation gives an additional proof for the suggested mechanism. Thus, at the later stages of stabilization (after the T_S), when the stabilizer residues act as HCl absorbers, the resulted amine salts being acidic in nature together with the acid chloride formed act as a strong catalyst for further degradation and consequently lead to increase in the extent of discoloration of the polymer.

The high stabilizing efficiency of the PACAH in the presence of 2 wt % DBLC (the concentration which is commonly used in industry), has directed our attention to study the effect of mixing PACAH with DBLC in the range of 0–100% of PACAH relative to DBLC. The overall mixed stabilizer concentration was kept constant at 2% based on the PVC weight. The results of the dehydrochlorination rate and the T_S values are illustrated in Figures 7 and 8, respectively. The results clearly reveal the greater stabilizing efficiency of these mixed stabilizers, and the existence of a true synergistic effect resulting from the combination of PACAH and DBLC which attained its maximum when the two additives are mixed in equivalent weight. It seems that the synergistic action resulted from the different mechanisms by which the PACAH (being a radical scavenger at the early stages of degradation) and DBLC work. Moreover, an additional proof for the observed synergistic effect resulted from the combination of the

two stabilizers (taken in different weight ratios) comes from the remarkable lowering in the extent of discoloration of the polymer when heated up to 30 min at 180°C, in air (Table III).

CONCLUSION

Poly(*N*-acryloyl-*N'*-cyanoacetohydrazide) (PACAH) has proved to be a good thermal stabilizer for rigid PVC when used alone or as a good costabilizer when mixed with DBLC. The observed synergistic effect when PACAH is mixed with DBLC arises from the different mechanisms by which the two stabilizers work.

References

1. McNeill, I. C.; Metmetea, I.; Cole, W. J. *Polym Degrad Stab* 1995, 49, 181.
2. Patel, K.; Velazquez, A.; Calderon, H. S.; Brown, G. R. *J Appl Polym Sci* 1992, 46, 179.
3. Bensemra, N.; Hoang, T. V.; Guyot, A. *Polym Degrad Stab* 1990, 28, 173.
4. Hjertberg, T.; Sorvik, E. M. *Polymer* 1983, 24, 673.
5. Hjertberg, T.; Sorvik, E. M. Report IUPAC Working Party on PVC; Cleavland, OH, 1980.
6. Panek, M. G.; Villacorta, G. M.; Starnes, W. H., Jr.; Plitz, I. M. *Macromolecules* 1985, 18, 1040.
7. Bauer, J.; Sabel, A. *Angew Makromol Chem* 1975, 47, 15.
8. Crawley, S.; McNeill, I. C. *J Polym Sci Polym Chem Ed* 1978, 5, 743.
9. Radiotis, T.; Brown, G. R. *J Macromol Sci Pure Appl Chem* 1997, 34, 743.
10. Dworkin, R. D. *J Vinyl Technol* 1989, 11, 15.
11. Simon, P.; Valko, L. *Polym Degrad Stab* 1992, 35, 249.
12. Gokcel, H. I.; Balkose, D.; Kokturk, U. *Eur Polym J* 1999, 35, 1501.
13. Tran, V. H.; Nguyen, Y. P.; Molinie, P. *Polym Degrad Stab* 1996, 53, 279.
14. Yassin, A. A.; Sabaa, M. W.; Mohamed, N. A. *Polym Degrad Stab* 1985, 13, 225.
15. Mohamed, N. A.; Sabaa, M. W. *Polym Int* 1998, 45, 147.
16. Sabaa, M. W.; Mohamed, N. A.; Oraby, E. H.; Yassin, A. A. *Polym Degrad Stab* 2002, 76, 367.
17. Sabaa, M. W.; Mohamed, R. R.; Yassin, A. A. *Polym Degrad Stab* 2003, 81, 37.
18. Sabaa, M. W.; Oraby, E. H.; Abdel-Naby, A. S.; Mohamed, R. R. *Polym Degrad Stab* 2006, 91, 242.
19. McNeill, M. C.; Neil, D. *Eur Polym J* 1970, 6, 134.
20. Dodson, B.; McNeill, I. C. *J Polym Sci Polym Chem Ed* 1976, 14, 353.
21. Mohamed, N. A.; Sabaa, M. W. *Eur Polym J* 1999, 35, 1731.
22. Naqui, M. K.; Sen, A. R. *Polym Degrad Stab* 1991, 33, 367.
23. McNeill, I. C.; Gorman, J. C. *Polym Degrad Stab* 1991, 33, 263.
24. McNeill, I. C.; Basan, S. *Polym Degrad Stab* 1993, 39, 139.
25. McNeill, I. C.; Basan, S. *Polym Degrad Stab* 1993, 39, 145.
26. McNeill, I. C.; Basan, S. *Polym Degrad Stab* 1993, 41, 311.
27. Mikheal, M. G. *Polym Degrad Stab* 1992, 36, 43.
28. Vymazal, Z.; Czako, E.; Meissner, B.; Stepek, J. *J Appl Polym Sci* 1974, 18, 2861.