

Inhibition of the Thermal Degradation of Rigid Poly(vinyl chloride) Using Poly(*N*-[4-(*N'*-phenyl amino carbonyl)phenyl]maleimide)

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ABSTRACT: Poly(*N*-[4-(*N'*-phenyl amino carbonyl)phenyl]maleimide), poly(PhPM), has been investigated for the inhibition of the thermal degradation of rigid poly(vinyl chloride) (PVC) in air, at 180°C. Its stabilizing efficiency was evaluated by measuring the length of the induction period, the period during which no detectable amounts of hydrogen chloride gas could be observed, and also from the rate of dehydrochlorination as measured by continuous potentiometric determination, and the extent of discoloration of the degraded polymer. The results have proved the greater stabilizing efficiency of poly(PhPM) relative to that of the DBLC commercial stabilizer. This is well demonstrated by the longer induction period values and by the lower rates both of dehydrochlorination and discoloration of the polymer during degradation relative to those of the DBLC reference stabilizer. The greater stabilizing efficiency of the poly(PhPM) is most probably attributed not

only to its possession of various centers of reactivity that can act as traps for radical species resulting during the degradation process, and replacement of labile chlorine atoms on PVC chains by relatively more thermally stable poly(PhPM) moieties, but also due to the ability of its fragmentation products to react with the evolved hydrogen chloride gas. A radical mechanism is suggested to account for the stabilizing action of this polymeric stabilizer. A synergistic effect is achieved when the poly(PhPM) was blended in various weight ratios with DBLC. This synergism attains its maximum when poly(PhPM) and DBLC are taken at 3 : 1 weight ratio. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2013–2018, 2010

Key words: poly(vinyl chloride); poly(*N*-[4-(*N'*-phenyl amino carbonyl)phenyl]maleimide); thermal dehydrochlorination; discoloration; costabilizer

INTRODUCTION

It is generally accepted that poly(vinyl chloride), PVC, is unstable when exposed to high temperatures during its molding and applications. The poor thermal stability of PVC is attributed to some structural defects formed during polymerization.^{1–6} The thermal degradation occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds.⁷ This in turn leads to unacceptable discoloration of the polymer and a drastic change in the physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain-scission or cross-linking, respectively.^{8–10} Aiming at the improvement of this thermal stability, many classes of the thermal stabilizers are used, such as, metallic soap stabilizers,¹¹ organotin stabilizers,¹² and metal-free and environmentally acceptable fully organic stabilizers.¹³ Different methods of using these stabilizers

are either addition to the polymer^{11–15} or chemical modification of the polymer to displace the labile sites by more stable stabilizer moieties.¹⁶ Grafting copolymerization¹⁷ or blending¹⁸ with other polymer of high thermal stability are the most recent methods. These last two methods possess the advantage that the stabilizing moieties are polymeric in nature which helps the compatibility between the polymer and the stabilizer moieties as well as the improvement of the mechanical properties.¹⁹ Maleimides were known to be of high thermal stability, because *N*-phenyl maleimide had been shown to be effective additive for the thermal stabilization of PVC.²⁰ Copolymers of *N*-phenyl maleimide with some vinyl monomers, such as, styrene, vinyl acetate, and methyl methacrylate were found to be of better thermal stability than the vinyl homopolymers and that the thermal stability increased as a function of the maleimide content.²¹ Moreover, Hoering et al.²² noticed that the glass transition temperature of vinyl chloride/*N*-phenyl maleimide copolymer increases linearly with increasing the maleimide content. Thermal stabilities of the copolymers of *N*-[4-(*N'*-phenyl amino carbonyl)phenyl]maleimide, (PhPM), with styrene and methylmethacrylate were much higher than those of *N*-phenyl maleimide/styrene and

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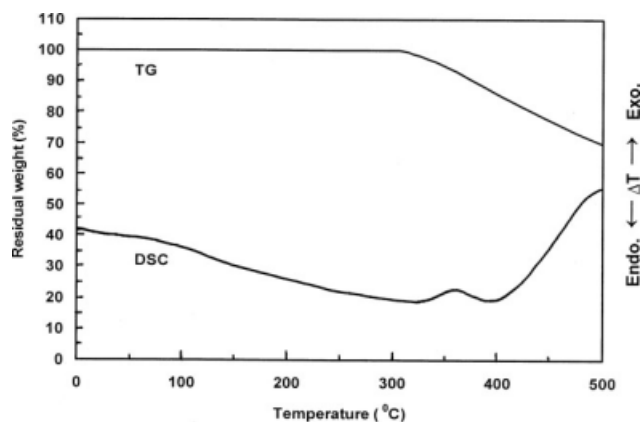


Figure 1 TG-DSC curves for poly(PhPM).

N-phenyl maleimide/methylmethacrylate copolymers.²³ Poly(*N*-[4-(*N*'-phenyl amino carbonyl)phenyl]maleimide), poly(PhPM), has excellent thermal stability because of a rigid backbone consisting of a five-membered ring structure (cyclic imide) as well as rigid thermally stable para-oriented phenylene rings and amide linkage as a substituent group.

In view of the aforementioned considerations, a trial has been made to improve the thermal characteristics of PVC using poly(PhPM) as additive. The attention has been confined to a low composition range from 0% to 5% poly(PhPM) based on the weight of PVC to keep the other characteristics of PVC unchanged.

EXPERIMENTAL

Materials

PVC (suspension) from the National Plastic Co. (Sabic, Kingdom of Saudi Arabia) with a *K*-value of 67; dibasic lead carbonate (DBLC) from the National Lead Co. (Germany) were used for this investigation.

Poly (*N*-[4-(*N*'-phenyl amino carbonyl)phenyl]maleimide), poly(PhPM), was prepared according to the method described by Oishi et al.²³ The prepared poly(PhPM) decomposed without showing glass transition temperature and the initial degradation temperature was over 320°C as indicated from its differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (Fig. 1). The DSC-TG thermograms were recorded on a Shimadzu DSC-50 and a Shimadzu TGA-50H in air at a flow rate of 20 mL/min and a heating rate of 10°C/min. Its molar mass was found to be 7500 g/mol as measured by gel permeation chromatography (GPC) on Agilent 1100 series (Germany), using THF as the eluent, PL gel particle size (5 μm), pore type (100, 10⁴, 10⁵ Å) on series, length 7.5 mm × 300 mm (1000, 5,000,000) and refractive index detector.

Preparation of PVC samples

PVC rigid samples were prepared according to the following recipe: PVC, 1 g; DBLC, 2 wt %; poly(PhPM), 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 comparable 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 gas. A detailed description of this method is given elsewhere.²⁴ A digital pH-meter (potentiometer) of the type CG-822 (Schott Gerade GmbH, Germany) was used. It was connected to a silver electrode and a saturated calomel reference electrode for the potentiometric measurement.

IR spectra were recorded using a Tescan Shimadzu Infrared Spectrophotometer (FTIR 8000, Japan) in the wave number range from 4000 cm⁻¹ to 600 cm⁻¹ at 25°C.

Elemental analyses were performed at the Micro-analytical unit, Cairo University.

Extent of discoloration of the degraded PVC samples was measured colorimetrically at λ = 500 nm as a function of degradation time using PerkinElmer UV/Visible Lambda 3 Spectrophotometer.

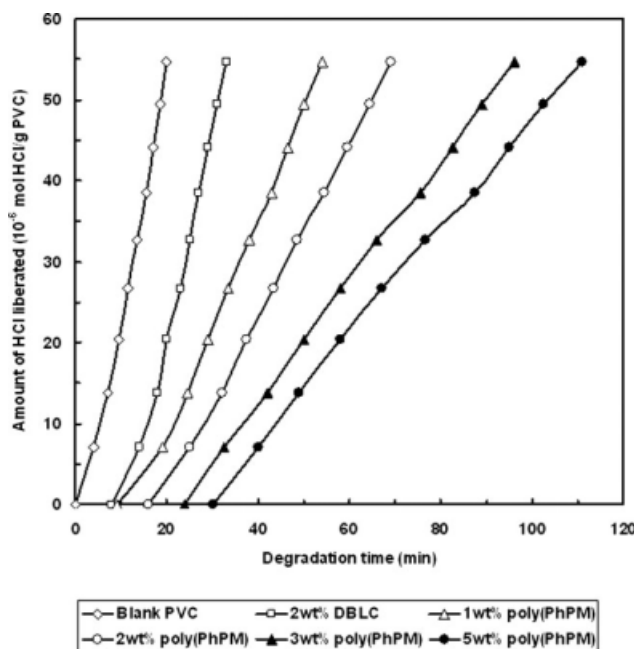


Figure 2 Induction period and rate of dehydrochlorination of rigid PVC degraded in air, at 180°C, in the presence of various concentrations of poly(PhPM).

RESULTS AND DISCUSSION

Results for the induction period values and the dehydrochlorination rates of rigid PVC degraded in air, at 180°C, in the presence of various concentrations of the polymeric additive poly(PhPM) are shown in Figure 2. The results for the nonstabilized blank sample as well as that for the sample stabilized by 2 wt % of DBLC are also given for comparison.

As shown from Figure 2, the results clearly reveal the appreciable improvement in the thermal stability of PVC stabilized by the investigated polymeric stabilizer poly(PhPM), and this improvement increases as a function of increasing the concentration of poly(PhPM) in the PVC samples. This appreciable improvement is demonstrated not only by the higher values of the induction period, which is the period during which no detectable amount of hydrogen chloride gas is liberated, but also by the lower rates of dehydrochlorination during the subsequent stages of the degradation reaction. Moreover, the results show the greater efficiency of the poly(PhPM) even at lower concentration (1 wt %) relative to that of the DBLC stabilizer (2 wt %).

Figure 3 represents the induction period values and the rates of dehydrochlorination of PVC samples stabilized with various concentrations of poly(PhPM) blended with 2 wt % of DBLC commercial thermal stabilizer when compared with the nonstabilized blank sample and that stabilized with 2 wt % DBLC. The results clearly reveal the remarkable improvement of both the induction period values and the rates of dehydrochlorination as a function of the increase of poly(PhPM) concentration.

The effect of adding poly(PhPM) in various concentrations to PVC samples in the absence and in the presence of 2 wt % DBLC on the extent of discoloration of the polymer at various time intervals is illustrated in Figures 4 and 5, respectively. The results show the low extent of discoloration of PVC samples stabilized with poly(PhPM) either in the absence (Fig. 4) or in the presence (Fig. 5) of DBLC as compared with the nonstabilized blank sample and sample stabilized with DBLC. The results also demonstrated a lower extent of discoloration of PVC sample stabilizer with a lower concentration of poly(PhPM) (1 wt %) relative to that of the sample stabilized with 2 wt % DBLC (Fig. 4).

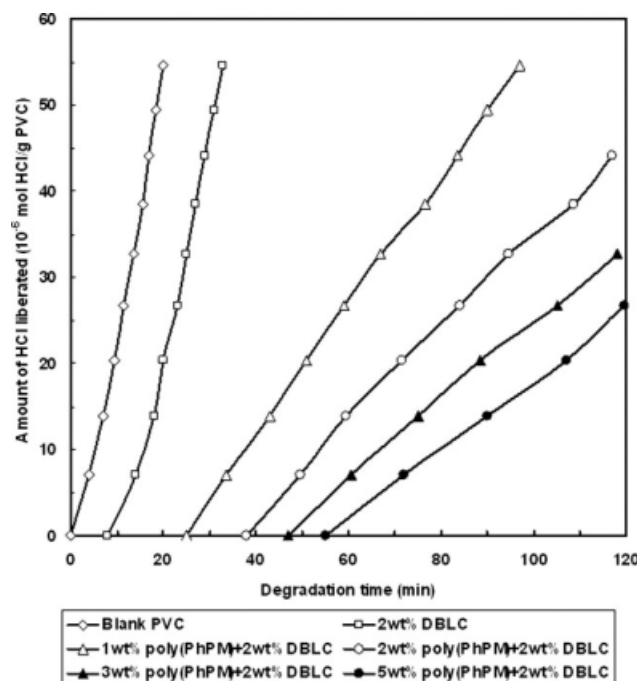
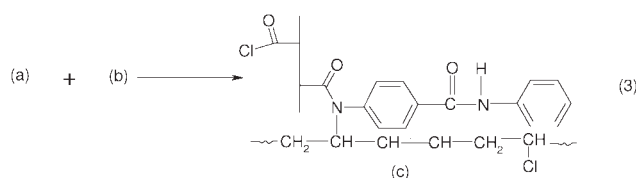
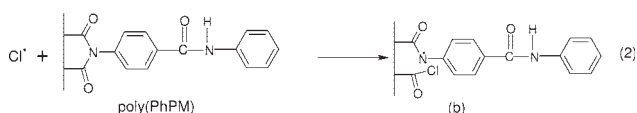
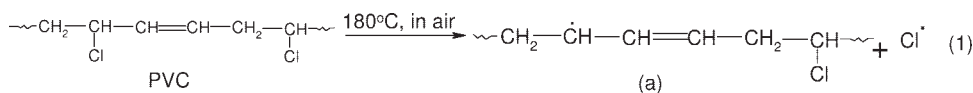
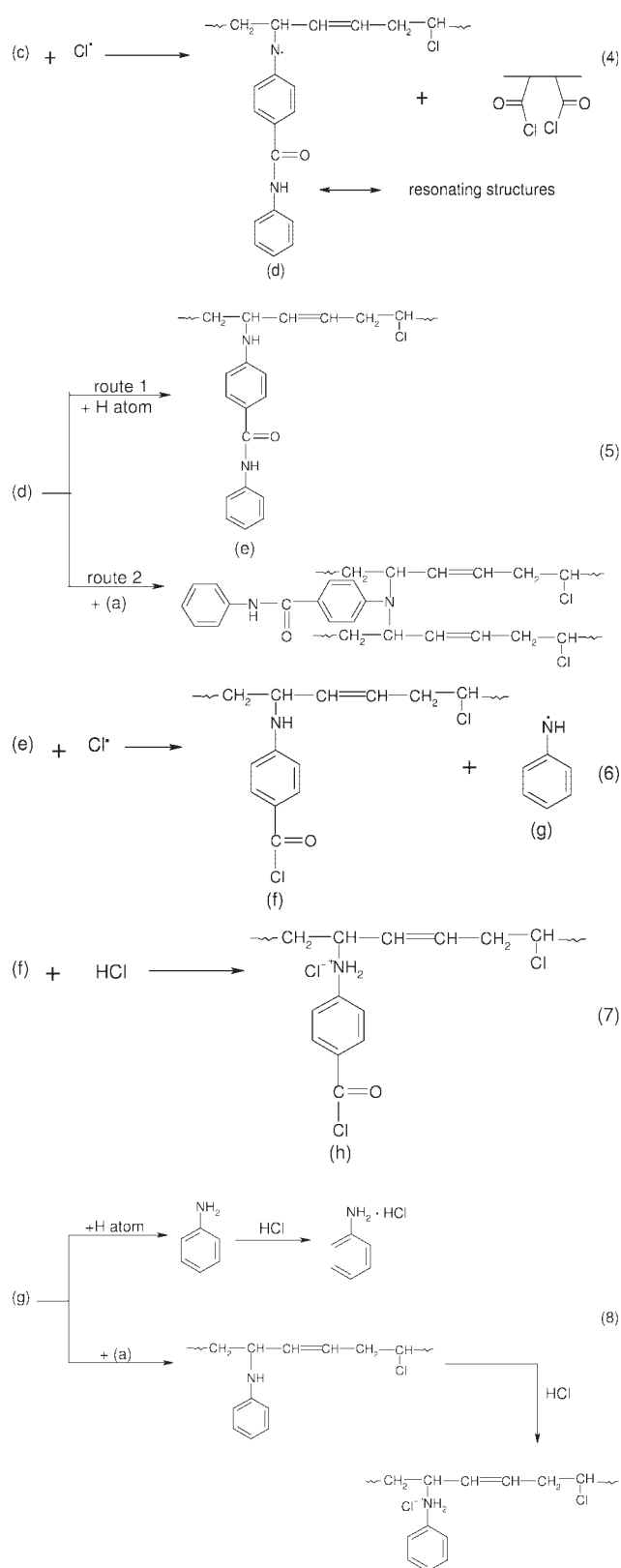


Figure 3 Induction period and rate of dehydrochlorination of rigid PVC degraded in air, at 180°C, in the presence of various concentrations of poly(PhPM) blended with 2 wt % DBLC commercial stabilizer.

poly(PhPM) (1 wt %) relative to that of the sample stabilized with 2 wt % DBLC (Fig. 4).

N-aryl maleimides have proved to be effective additives for stabilization of PVC against thermal degradation.²⁰ They exhibited their stabilizing efficiency both through the replacement of the labile chlorine on PVC chain by a relatively more thermally stable stabilizer moiety and through effective absorption of the liberated hydrogen chloride gas. Their stabilizing efficiency is attributed to their radical trapping potency, which intervenes with the radical degradation process of PVC. This most probably occurs not only through trapping the radical species in the degradation process but also by blocking the radical sites created on the polymer chains. In view of some structural similarity of poly(PhPM) to *N*-aryl maleimides, the stabilization mechanism of poly(PhPM) would be expected to be analogous to that of *N*-aryl maleimides and may be represented as follows:





To give evidences for this mechanism, a series of experiments has been made by following the IR spectra of PVC samples stabilized by the polymeric additive poly(PhPM) and degraded in air, at 180°C, for various time intervals (0, 15, 30, 45, 60, and 80) (Fig. 6). In these experiments, poly(PhPM) was used

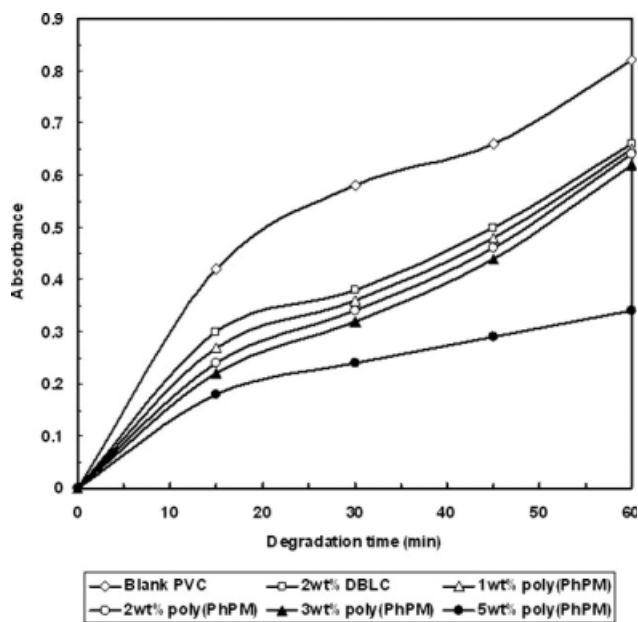


Figure 4 Extent of discoloration of rigid PVC degraded in air, at 180°C, in the presence of various concentrations of poly(PhPM) as a function of degradation time.

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 hot acetone and chloroform to remove any residual unreacted poly(PhPM) and its fragments.

The results of the FTIR spectra at the early stages of degradation show the presence of absorption bands at 690, 760, 830, and 1599 cm⁻¹ which indicate the presence of an aromatic moiety, at 1680 cm⁻¹: corresponding to the amide carbonyl group, at 1730 cm⁻¹: characteristic for the presence of the imide carbonyl group, and at 3290 cm⁻¹: assigns to the NH group. However, at subsequent stages of degradation (45–60 min), the FTIR spectra show a gradual disappearance of the band corresponding to the imide carbonyl group. At the later stages of degradation (80 min), the IR spectra show a disappearance of the band corresponding to the amide carbonyl group together with the appearance of two new absorption bands at 1820 cm⁻¹ and 1640 cm⁻¹ corresponding to the carbonyl group of the acid chloride (O=C–Cl) and the conjugated carbon–carbon double bonds created on the degraded PVC chains, respectively. Moreover, the new band at 1500 cm⁻¹ which corresponds to the formation of quaternary ammonium salt and which appears at the later stages of degradation gives an additional proof for the possibility of this polymeric stabilizer to act as an hydrogen chloride gas absorber. The elemental analyses have shown that nitrogen is present in the aforementioned degraded PVC residues. This result coupled with the IR results indicates that poly(PhPM) molecule or at least a part of

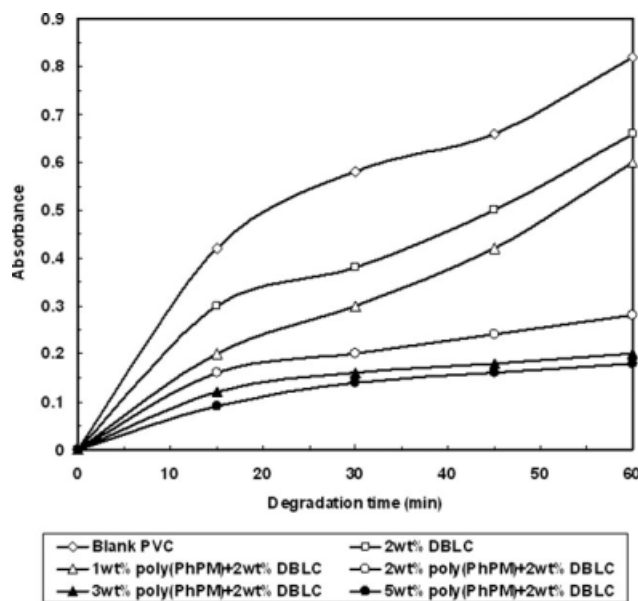


Figure 5 Extent of discoloration of rigid PVC degraded in air, at 180°C, in the presence of various concentrations of poly(PhPM) blended with 2 wt % DBLC as a function of degradation time.

it is chemically bonded to the PVC matrix during the stabilization process.

According to the suggested mechanism, the labile chlorine atom detached from the PVC chain [eq. (1)] is trapped by the poly(PhPM) molecule through its imide linkage resulting in the formation of poly(PhPM) radical [eq. (2)]. Once formed, the poly(PhPM) radical blocks the radical site on the PVC chain, thus disrupting the radical chain degradation of PVC [eq. (3)]. On the other hand, the decrease in the intensity of the imide linkage (IR peak at 1730 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 linkage of the poly(PhPM) already attached to the PVC leading to its cleavage [eq. (4)]. Moreover, Route 1 of eq. (5) seems to be the most probable as no crosslinks for the degraded PVC samples containing the polymeric stabilizer were observed because the degraded PVC samples were completely soluble in tetrahydrofuran. Further, the disappearance of the amide linkages (IR peak at 1680 cm^{-1}) together with the appearance of a new band at 1820 cm^{-1} , which corresponds to the carbonyl group of the acid chloride, support the eq. (6) of the proposed mechanism. However, eqs. (7) and (8) represent another possibility of stabilization at the later stages of degradation of PVC through the absorption of the evolved hydrogen chloride gas by the basic groups of the already attached poly(PhPM) moiety.

The high stabilizing efficiency of poly(PhPM) in the presence of 2 wt % DBLC (the concentration which is commonly used in industry) has directed my attention to study the effect of mixing poly(PhPM) with DBLC in

the range of 0–100% of poly(PhPM) relative to DBLC. The overall mixed stabilizers concentration was kept constant at 2% based on the PVC weight. The results of the induction period values and the rates of the dehydrochlorination are represented in Figure 7. The results clearly reveal the greater stabilizing efficiency of these mixed stabilizers, and the existence of a true synergistic effect resulting from combination of poly(PhPM) and DBLC which attained its maximum at 3 : 1 wt % of poly(PhPM)/DBLC.

The observed synergistic effect is most probably attributable to the combination of the mechanisms by which the poly(PhPM) and the DBLC work. Thus, when poly(PhPM) works through radical trapping and blocking the radical sites on the PVC chains (at the early stages of degradation) and neutralizing the evolved hydrogen chloride gas (at the later stages of degradation), the DBLC only neutralizes the hydrogen chloride gas liberated.

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 60 min at 180°C, in air (Fig. 8). Thus, the use of poly(PhPM) as a

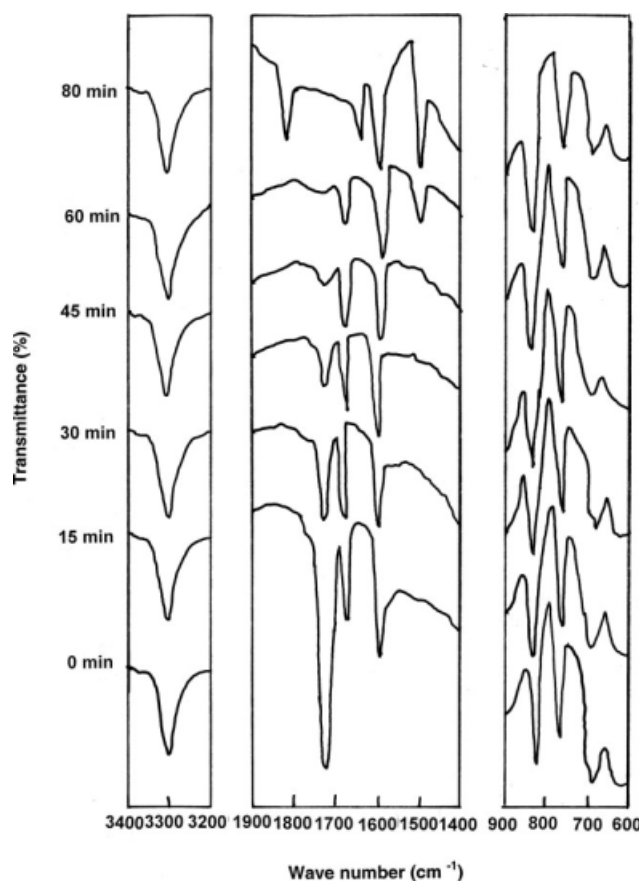


Figure 6 Changes in the FTIR spectra for rigid PVC samples degraded in air, at 180°C, in the presence of poly(PhPM) as a function of degradation time.

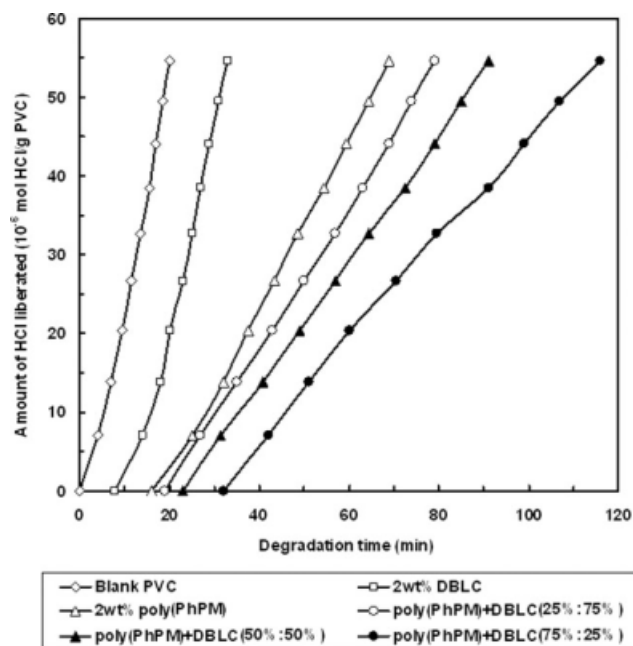


Figure 7 Induction period and rate of dehydrochlorination of rigid PVC degraded in air, at 180°C, in presence of various weight ratios of poly(PhPM) mixed with DBLC. All mixed stabilizers concentration was kept constant at 2% based on the weight of PVC.

co-stabilizer with the industrially known stabilizer DBLC is very important as a part of DBLC could be substituted by a much safer stabilizer, thus lowering its toxicity, if it is indeed present.

CONCLUSIONS

Poly(PhPM) has proved to be a good thermal stabilizer for rigid PVC when used alone or as a

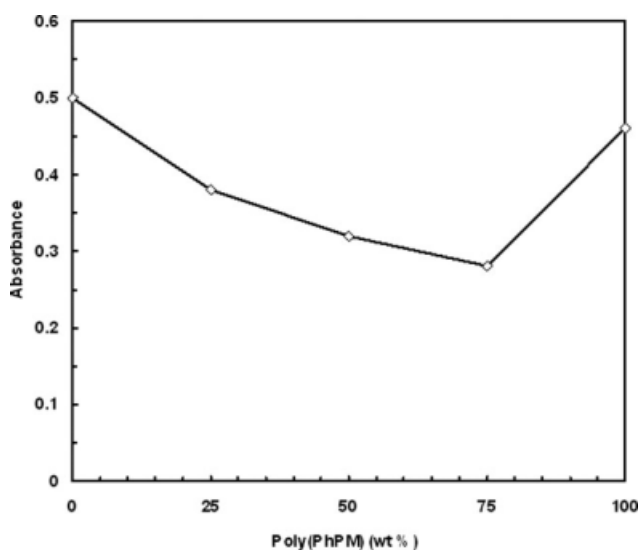


Figure 8 Extent of discoloration of rigid PVC degraded in air, at 180°C, for 60 min in the presence of various weight ratios of poly(PhPM) mixed with DBLC. The overall mixed stabilizers concentration was kept constant at 2% based on the weight of PVC.

good co-stabilizer when mixed with DBLC commercial stabilizer. The greater stabilizing efficiency of poly(PhPM) relative to that of DBLC is illustrated by longer induction period value, slower rate of dehydrochlorination, and lower extent of discoloration. Poly(PhPM) can act as a scavenger for chlorine radicals resulting from the degradation of PVC and has the ability to block the odd electron sites that may be created on PVC chains as a result of thermal degradation. Also, it has the ability to intervene in the degradation process as a strong hydrogen chloride gas absorber, thus protecting the polymer from the deleterious effect of this acidic degradation promoter. A true synergistic effect is observed when the poly(PhPM) is mixed with DBLC in different proportions. The maximum synergism was obtained at 3 : 1 weight ratio of poly(PhPM) : DBLC. The observed synergistic effect arises from the different mechanisms by which the two stabilizers work.

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