

Thermal Degradation Behavior of Poly(vinyl chloride) in the Presence of Poly(glycidyl methacrylate)

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ABSTRACT: The thermal degradation behavior of poly(vinyl chloride) (PVC) in presence of poly(glycidyl methacrylate) (PGMA) has been studied using continuous potentiometric determination of the evolved HCl gas from the degradation process from one hand and by evaluating the extent of discoloration of the degraded samples from the other. The efficiency of blending PGMA with dibasic lead carbonate (DBLC) conventional thermal stabilizer has also been investi-

gated. A probable radical mechanism for the effect of PGMA on the thermal stabilization of PVC has been suggested based on data reported by FTIR and elemental analyses. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2205–2210, 2008

Key words: poly(vinyl chloride); poly(glycidyl methacrylate); thermal dehydrochlorination; discoloration; stabilization mechanism; costabilizer

INTRODUCTION

There is a general agreement that poly(vinyl chloride) (PVC) thermal ageing occurs by autocatalytic dehydrochlorination reaction which involves the sequential loss of hydrogen chloride molecules accompanied by the generation of conjugated polyene sequences.¹ This in turn leads to an 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 crosslinking, respectively.^{2–4}

Various defect sites in the polymer chain are thought to be responsible for this instability. Possible defect structures in PVC chains are allylic chlorine,⁵ tertiary hydrogen and chlorine atoms,⁶ terminal end groups such as double bonds,⁷ oxygen containing groups,⁸ or peroxide residues,⁹ head-to-head structures,¹⁰ and steric order of the monomer (tacticity).¹¹ Thus, stabilization of PVC against thermal degradation is essential for its processing and use at high temperatures. The thermal stabilizers commonly in use for the stabilization of PVC are either basic salts¹² which can react with the evolved hydrogen chloride gas, thus retarding its deleterious catalytic action,¹³ metallic soaps,¹⁴ and esters or mercaptides of dialkyl tin¹⁵ 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.¹⁶ Stabilizers of an organic nature have recently been established for the thermal stabilization of PVC.^{17–20} Blending 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),²¹ poly(styrene),²² poly(vinyl butyral),²³ and *cis*-poly butadiene²⁴ or step growth polymers like poly(tetra methylene sebacate),²⁵ poly(dimethylsiloxane),²⁶ bisphenol-A polycarbonate,²⁷ and poly(ethylene adipate).²⁸

In our previous paper, poly(*N*-acryloyl-*N'*-cyanoacetohydrazide) has proved a good thermal stabilizing efficiency for rigid PVC when used alone or as a costabilizer with dibasic lead carbonate a widely used commercial thermal stabilizer.²⁹ Epoxy compounds, as costabilizers, in conjunction with heavy metal carboxylates have also been used for stabilization of PVC against thermal degradation.^{30,31} However, the epoxy compounds act as HCl absorbers, the heavy metal carboxylates can exchange the labile chlorine in the PVC molecules by more stable ester groups. Thus, it became of interest to study the thermal characteristics of PVC in the presence of poly(glycidyl methacrylate) (PGMA) which combine the characteristics of both the epoxide and ester groups in its structure. Our attention has been confined to a low composition range from 0 to 5% of PGMA based

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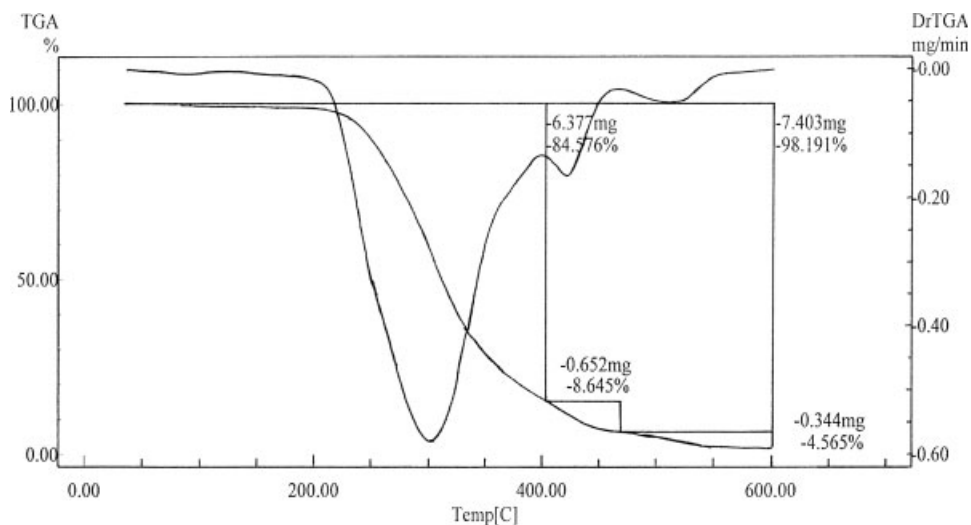


Figure 1 Thermogravimetric analysis (TG) of PGMA in air atmosphere.

on 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.

Poly(glycidyl methacrylate), PGMA, was prepared according to the method described by Eckert et al.³² The prepared PGMA is thermally stable till 200°C as indicated from its thermogravimetric (TG) analysis (Fig. 1). The TG thermogram was recorded on a Shimadzu TGA-50H in air at a flow rate 20 mL/min and a heating rate of 10°C/min. Its molar mass was found to be ~ 61,000 g/mol as measured by eligent GPC, Germany, PL, Gel, 5 μ m, 100, 10⁴, 10⁵ Å on serial reflective index detector.

Preparation of PVC samples

PVC rigid samples were prepared according to the following recipe: PVC, 1 g; DBLC, 2 wt %; PGMA, 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 descrip-

tion of this method is given elsewhere.³³ 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.

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 Microanalytical unit, Cairo University.

RESULTS AND DISCUSSION

Results of dehydrochlorination rates of rigid PVC thermally degraded at 180°C, in air, in the presence of various concentrations of the polymeric additive PGMA blended with 2 wt % of dibasic lead carbonate (DBLC) commercial thermal stabilizer are shown in Figure 2. Results of a nonstabilized blank sample

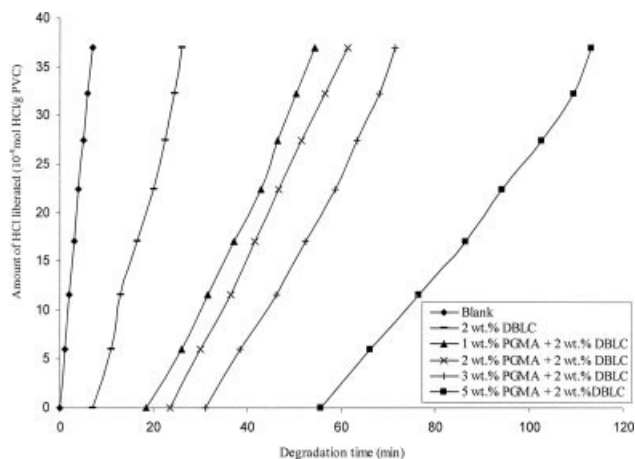


Figure 2 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in the presence of 2 wt % DBLC commercial stabilizer blended with various concentrations of PGMA.

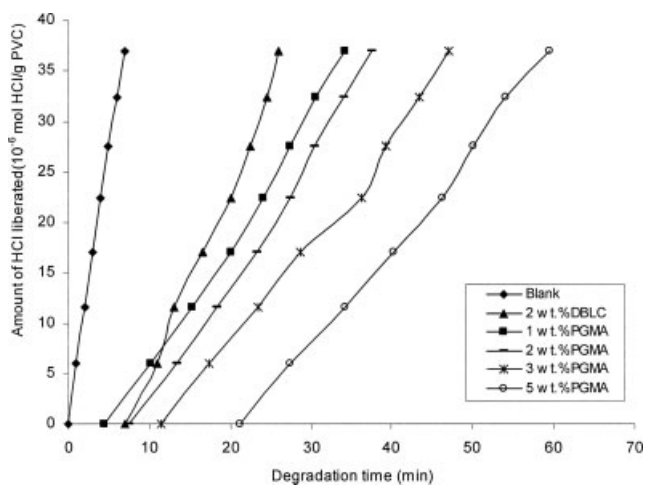


Figure 3 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in the presence of various concentrations of PGMA.

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 (PGMA), and this improvement increases as a function of increasing the concentration of PGMA in the PVC samples. This remarkable improvement is illustrated not only by the presence of a well defined thermal stability values (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 (Fig. 2).

Figure 3 represents the rates of dehydrochlorination of PVC samples stabilized with various concentrations of PGMA used alone as thermal stabilizers (i.e., in absence of DBLC) when 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 PGMA concentration. Moreover, the results also demonstrate the slower rate of dehydrochlorination of PVC sample stabilized with 2 wt % of PGMA when compared with the same concentration of DBLC. However, both of these two samples showed a comparable T_s values.

To suggest a probable mechanism for the stabilizing action for PGMA, a series of experiments has been made by following the IR spectra of PVC samples stabilized by the polymeric additive and thermally degraded at 180°C, in air, for different time intervals (from 10 to 60 min) (Fig. 4). In these experiments, PGMA 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 chloroform to remove any residual unreacted PGMA and its fragments. The results show the appearance of only one new band at 1729 cm^{-1} which corresponds to the carbonyl of the ester group of the polymeric additive. This result indicates that PGMA or a part of it is chemically bound to the PVC chains. Thus, the labile chlorine atom detached from the PVC chain molecule [eq. (1)] is trapped by PGMA molecule resulting in the formation of epichlorohydrin and methacryloyl oxy radical [eq. (2)]. The latter blocks the radical site on the PVC chain, thus disrupting the radical chain degradation of PVC [eq. (3)]. This conclusion is supported earlier by the finding of Johnston et al.³⁴ and later by Sundbq et al.³⁵ Moreover, the partial gelation of degraded PVC samples containing the polymeric stabilizer gives an additional proof for eq. (3).

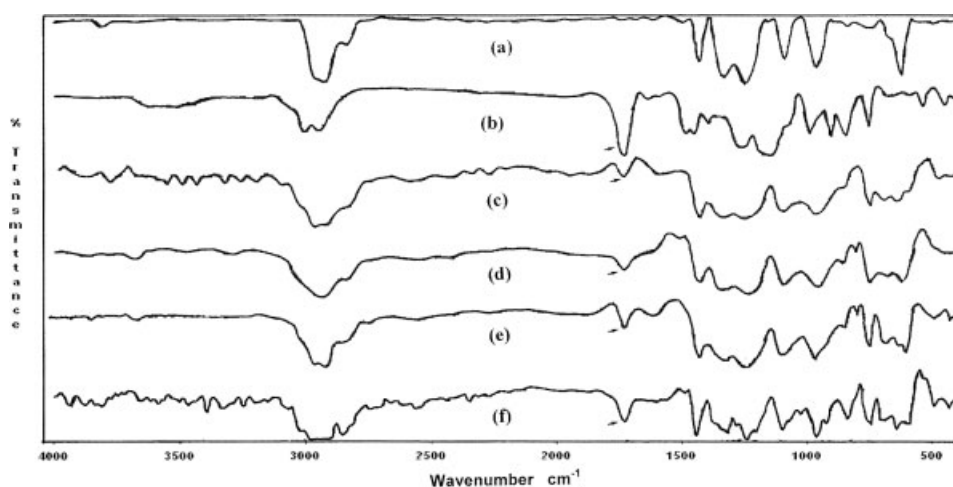


Figure 4 Change in the IR spectra of PVC samples degraded at 180°C, in air, in the presence of PGMA as a function of degradation time: (a) blank PVC, (b) PGMA, (c) 10 min, (d) 20 min, (e) 40 min, (f) 60 min.

chloride gas over a sample of PGMA in the degradation tube at 180°C, in air, for 30 min. The IR spectrum (Fig. 5) of the obtained product showed the disappearance of the epoxide stretching band at 906 cm^{-1} , together with the appearance of $-\text{OH}$ stretching band at 3600–3100 cm^{-1} and $\text{C}-\text{Cl}$ stretching band at 763 cm^{-1} .

Moreover, the elemental analysis has proved the presence of chlorine in the HCl-treated sample. This supports that PGMA has the ability to interact with the eliminated HCl through opening its epoxide rings.

The true synergistic effect observed when the investigated polymeric stabilizer is added to DBLC commercial stabilizer is most probably due to the two different mechanisms by which the two stabilizers work. The former acts as a radical trap and as HCl absorber, whereas the latter acts only as HCl absorber.

The high stabilizing efficiency of PGMA in presence of 2 wt % DBLC (the concentration which is commonly used in industry), has directed our attention to study the effect of mixing PGMA with DBLC in the range of 0–100% PGMA 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 represented in Figures 6 and 7, respectively. The results clearly reveal the greater stabilizing efficiency of these mixed stabilizers, which give an additional proof for the existence of a true synergistic effect resulting from the combination of PGMA and DBLC which attained its maximum when the two additives are mixed in equivalent weight.

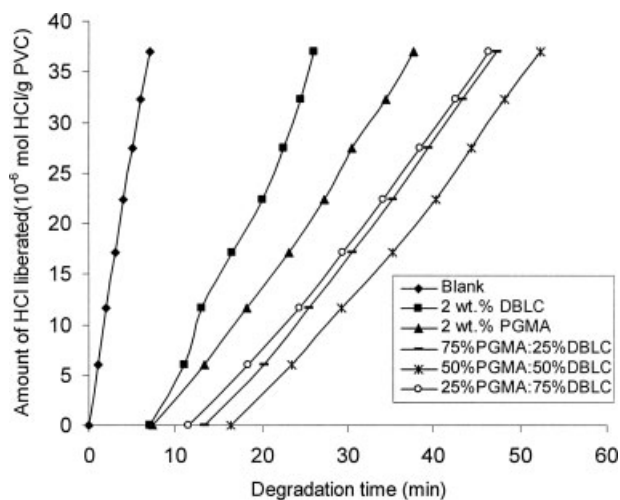


Figure 6 Rate of dehydrochlorination of rigid PVC at 180°C, in air, in the presence of various weight ratios of PGMA mixed with DBLC. The overall mixed stabilizers concentration was kept constant at 2% based on the weight of PVC.

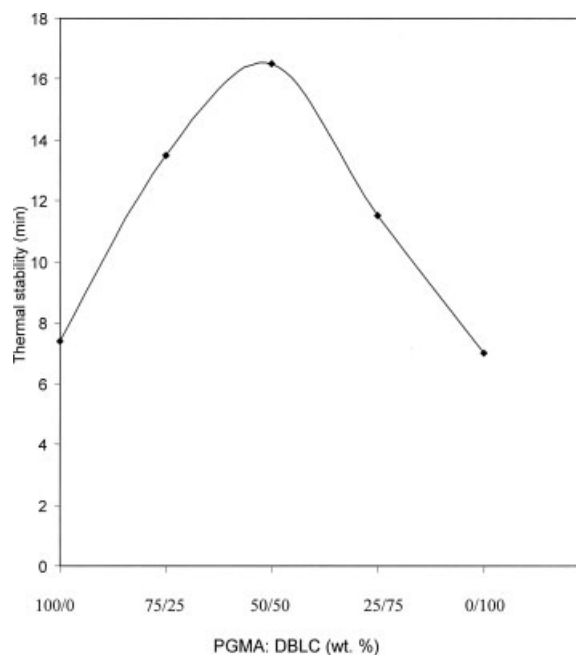


Figure 7 Thermal stability (T_s) composition curve for PGMA and DBLC mixtures.

CONCLUSION

PGMA has proved to be a good thermal stabilizer for rigid PVC when used alone or when mixed with dibasic lead carbonate (DBLC). The improvement is illustrated not only by the increase in the thermal stability values, but also by the slow rate of dehydrochlorination as compared with the blank or the reference stabilizer when used alone. Moreover, the observed synergistic effect when PGMA is mixed with DBLC arises from the different mechanisms by which the two stabilizers work.

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