

## Stabilizing Effect of Organic Stabilizer (EDTA, 1,2 Propane diol, Benzoic Acid and Phenol) on the Thermal Degradation of Polyvinyl Chloride (PVC)

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### Abstract

Organic stabilizers have been investigated as thermal stabilizers for rigid polyvinyl chloride (PVC) at 180°C in inert atmosphere by measuring the rate of dehydrochlorination and changes in intrinsic viscosity, UV absorption spectra, FT-IR spectra and levels of unsaturation in the degraded polymer samples have been used to assess the effects of the materials on the degraded polymer. Their stabilizing efficiencies are based on measuring the length of the induction period ( $T_S$ ), the period during which no detectable amounts of HCl gas could be observed, and also from the rate of the dehydrochlorination as measured by bromometry titration on the one hand, and the extent of discoloration of the degraded polymer samples on the other. The results revealed the greater stabilizing efficiencies of the investigated materials as shown by their longer induction periods ( $T_S$ ) and by the lower dehydrochlorination rate in relation to blank PVC. The stabilizer efficiency attributed to the replacement of the labile chlorine on the PVC chains by a relatively more thermally stable aromatic and aliphatic moiety. A radical mechanism for the stabilizing action of the investigated stabilizers is offered. A synergistic effect achieved when the material under investigation were blended in 1:1 weight ratio with either. The results reveal that mixing of the stabilizers improves the  $T_S$  values, the rate of dehydrochlorination and the extent of discoloration.

**Keywords:** Polyvinyl chloride; Thermal dehydrochlorination; Thermal degradation; Organic stabilizers; Mixed stabilizers

### 1. Introduction

It is generally accepted that poly vinyl chloride (PVC) is an unstable polymer when exposed to high temperatures during its mouldings and applications. Therefore, the poor thermal stability of PVC still

remains one of its main problems. At elevated temperatures, well below its melting point, PVC loses HCl and becomes discolored. Because these changes are associated with a deleterious in some of the useful properties of the polymer, it has become the practice to process PVC in the presence of heat stabilizers. The

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poor thermal stability of PVC requires the use of stabilizers in processing. Additives that have found practical application as thermal stabilizers for PVC include metal salts of organic acids, organometallic compounds and inhibitors of radical chain reactions. Several workers [1-5] have reported on the degradation and stabilization of PVC. Various defect sites in the polymer chain are thought to be responsible for this instability. Possible defect structures in PVC are allylic chlorine [6,7], tertiary hydrogen and chlorine atoms associated with branches [8], terminal end groups such as double bonds [9], oxygen containing groups [8-10], peroxide residues [11], head to head structures. In addition to these abnormalities the steric order of the monomer units in the polymeric chain (tacticity) may have some influence on the degradation [12-14]. Thus, stabilization of PVC against thermal degradation is essential for its processing and use at high temperatures. The adopted stabilization accordingly involves intervention with the dehydrochlorination process and reaction with the double bonds created on the backbone chains as a result of hydrogen chloride loss during degradation. Thermal degradation of PVC is generally considered to be initiated at unstable sites within the structure of the polymer [15-18]. This results in an unacceptable discoloration of the polymer and a drastic change in its mechanical properties [19]. Thermal stabilizers are known to function by replacing labile atoms in PVC; the inhibitor suppresses the elimination of HCl and interrupts the formation of conjugated polyene sequence in the polymer [1]. Common thermal stabilizers in use for the stabilization of PVC are usually either basic lead salts [20] which can react with the evolved hydrogen chloride gas to retard the deleterious catalytic action of the eliminated hydrogen chloride [21,22], metallic soaps [23-26] and esters or mercaptides of dialkyltin [27-29] that can exchange the labile chlorines in the backbone chains for more stable ester or mercaptide groups derived from the stabilizer. Moreover, quinone-tin polymers act as stabilizers through intervention in the radical process of degradation and through effective absorption of the degradation products [30]. Moreover, the stabilizer may function by disruption of the conjugated systems, thus reducing the discoloration of the polymer. Mercaptans are typical examples of these stabilizers [31]. However, irrespective of their stabilizing efficiencies, they suffer from the deleterious effect of their by products, mostly metal chlorides, accumulated during the reaction of these stabilizers with the polymeric chains. These metal chlorides are considered as strong catalysts for the subsequent dehydrochlorination process, and they are responsible for the sudden blackening of certain

formulations, and may present a serious environmental problem [32,33]. This has led, recently, to the extensive use of stabilizers of an organic nature for the thermal stabilization of PVC [34,35]. The present study was undertaken and directed towards their investigations as thermal stabilizers for rigid PVC. Some organic compounds namely ethylene diamine tetra acetic acid (EDTA), 1,2 propane diol, benzoic acid and phenol were used.

## 2. Experimental

### 2.1. Materials

A suspension PVC with  $M_r = 48000$ ,  $k$ -value = 55-57; from Fluka Company; EDTA; benzoic acid, 1,2 propane diol and phenol from Merck company were used for this investigation. PVC was purified by solution in THF / acetone mixture and precipitated with constant stirring, in a large excess of methanol. The precipitated polymer was filtered off after 24 h, washed with methanol, and air-dried [36].

### 2.2. Degradation of PVC

Rates of dehydrochlorination degradation studies were carried out using PVC powder in the presence of organic stabilizer at 180°C under nitrogen atmosphere. The PVC sample (0.2 g) was mixed thoroughly with an appropriate amount of additive (0.006 g) and transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 180 ml/min. The degradation tube was immersed in a thermostat oil bath controlled. The amount of HCl evolved was established after various periods of time by titration. The extent of dehydrochlorination (% conversion) was calculated from the ratio of HCl evolved to the amount available in the polymer [37].

### 2.3. Intrinsic Viscosity Measurements

A portion of the degraded PVC was purified by solution in cyclohexanone and precipitated in a large excess of methanol. The precipitated polymer was filtered off, washed several times with methanol, dried in vacuum at room temperature and stored in the dark. Intrinsic viscosities were determined from measurements in cyclohexanone solution at 30°C. The intrinsic viscosities were determined using the relationship:

$$[\eta] = (\eta_{sp} + 3 \text{Ln } \eta_{rel}) / 4C \quad (1-2)$$

$$\eta_{rel} = \eta / \eta_0 = t / t_0 \quad (2-2)$$

$$\eta_{sp} = \eta_{rel} - 1 \quad (3-2)$$

where  $[\eta]$ ,  $\eta_{sp}$  and  $\eta_{rel}$  are the intrinsic, specific and relative viscosities, respectively and  $C$  is the concentration of the solution (g/ml). In these expressions,  $t$  is the time of flow of polymer solution and  $t_0$ , the time of flow of solvent at the temperature of measurement. The ratios of the intrinsic viscosity of PVC samples degraded in the presence of additives to the viscosity of undegraded sample. ( $[\eta]/[\eta_0]$ ) was used to deduce the effect of the additives on the degradation of PVC.

#### 2.4. The Levels of Unsaturation in the Degraded PVC

The polymer was dissolved in 1,2 dichloroethane and solution of bromine in carbon tetrachloride, somewhat in excess, was added. After remaining for 24 h in darkness at ambient temperature the unreacted bromine was estimated by adding aqueous potassium iodide and measuring the iodine liberated by titration with sodium thiosulphate [38].

#### 2.5. UV-visible Absorption by Degraded Samples

Shimadzu 120-02UV/visible spectrophotometer was used in the analysis of degraded polymer samples in 1, 2 dichloroethane solution for conjugated double bonds. The degraded PVC samples dissolved readily in warm 1,2 dichloroethane. The extent of discoloration of the degraded polymer samples was measured colorimetrically at  $\lambda=360$  nm as a function of the degradation time.

#### 2.6. FT-IR Spectra

IR spectra were recorded by Fourier transform infrared spectrophotometer (FT-IR) using the FT-IR shimadzu model 4300 Japan in the range  $650-4000\text{ cm}^{-1}$  at  $25^\circ\text{C}$ . All the samples were mixed with KBr for these analyses.

### 3. Results and Discussion

#### 3.1. Stabilization of Thermally Degraded Rigid PVC Using Organic Acids and Alcohols

Results of the dehydrochlorination (% conversion) of rigid PVC stabilized by organic acids and alcohols against thermal degradation, effected at  $180^\circ\text{C}$  in inert atmosphere, are represented in Figure 1. It can be seen from this figure that the investigated compound exhibits a greater stabilizing efficiency compared to that of PVC blank. The greater stabilizing efficiency is illustrated not only by lower rates of dehydrochlorination during the subsequent stages of degradation reaction, but also by

the longer induction periods ( $T_S$ ) during which no detectable amounts of hydrogen chloride gas are liberated (Tables 1 and 2). The introduction of OH and  $\text{CO}_2\text{H}$  groups into the phenyl ring and, other materials of the stabilizer resulted in an appreciable improvement in both  $T_S$  and the rate of dehydrochlorination. This fact confirms the important role played by OH and  $\text{CO}_2\text{H}$  groups in the phenyl ring and other materials of the stabilizer in the stabilization mechanism. The results show that the EDTA is more effective than the others. It seems that the order of increasing stabilization effectiveness is EDTA > 1,2 propane diol > Benzoic acid > Phenol.

#### 3.2. Stabilization of Thermally Degraded Rigid PVC Using Mixed Stabilizer

The results of the dehydrochlorination of thermally degraded rigid PVC at  $180^\circ\text{C}$  in  $\text{N}_2$  in the presence of the mixed stabilizers are shown in the Figure 2. The results clearly reveal the greater stabilizing efficiency of these mixed stabilizers, reaching its maximum when the two stabilizers were mixed in a 1:1 ratio, respectively.

#### 3.3. Extent of Thermal Degradation: Intrinsic Viscosity

The variation in the values of relative intrinsic viscosities  $[\eta]/[\eta_0]$ ; where  $[\eta_0]$  is the intrinsic viscosity of undegraded polymer; and  $[\eta]$  is the intrinsic viscosity of the degraded PVC samples with degradation time are shown. The major types of reactions that may take place during the thermal degradation of PVC in  $\text{N}_2$  at moderate temperatures such as dehydrochlorination, polymer chain scission, cross-linking, would influence the viscosity of the degraded polymer samples. It has been reported that the intrinsic viscosity of PVC undergoing degradation decreases initially to a minimum and then increases with further increase in the number of double bonds in the polymer [39], probably due to reduced flexibility along the main polymer chain. Therefore, in low extents of degradation, it can be assumed that reactions accompanying dehydrochlorination are negligible and that the values of intrinsic viscosity represent the extent of degradation; the lower the values of intrinsic viscosity, the greater the extent of degradation. The results in Figure 3 show that the values of intrinsic viscosity obtained for PVC samples degraded in the presence of stabilizers are much higher than the values for the unstabilized PVC samples. These results are indicative of a stabilizing effect of the materials on the thermal degradation of PVC.

**Table 1.** The induction period as a function of the type of the stabilizer investigated in the 180°C with 0.2 g PVC and various concentration of stabilizer

Stabilizer Concentration (g)	EDTA Ts (min)	1,2 Propane diol Ts (min)	Benzoic Acid Ts (min)	Phenol Ts (min)
0.008	20	19	16	13
0.007	19	18	15	12
0.006	18	17	14	11
0.005	15	14	12	10
0.004	12	10	8	7
0.003	9	8	6	5
0.002	7	5	4	2

**Table 2.** The induction period as a function of the type of stabilizer investigated with constant concentration of stabilizer in various temperature

Stabilizer T(°C)	EDTA Ts (min)	1,2 Propane diol Ts (min)	Benzoic Acid Ts (min)	Phenol Ts (min)	Non Ts (min)
160	25	23	22	20	10
165	23	21	20	18	7
170	22	20	18	15	5
175	19	16	14	13	3
180	17	14	12	11	2
190	12	10	9	8	1

### 3.4. Levels of Unsaturation in Degraded PVC Samples: Bromometry

The evolution of HCl during thermal degradation of PVC leads to the formation of double bonds in the polymer. Therefore, provided that in the presence of stabilizer the extent of degradation is low, and that the double bonds formed during the initial stage of dehydrochlorination do not undergo further reactions, measurement of bromine value consumed of degraded PVC samples should provide satisfactory estimate of the extent of degradation.

The numbers of double bonds in the degraded polymer samples were worked out from the bromine values consumed and are shown in the Figure 4 as a function of degradation time. The results show that the amount of Br<sub>2</sub> consumed in the samples degraded, in the presence of these stabilizers, is smaller than the level of unsaturation in the unstabilized polymer samples. As with the results obtained from viscosity measurements, the EDTA is more effective than the other stabilizers in the thermal stabilization of PVC.

### 3.5. FT-IR Spectra of Degraded PVC Samples

In order to examine the effects of organic stabilizer on PVC degradation by FT-IR spectroscopy, films of appropriate thickness to give adequate absorption in the required range were prepared. The FT-IR spectra of undegraded PVC unstabilized degraded PVC and degradation PVC in the presence of stabilizer are shown in Figures 5-7, respectively. In this study attention was focussed on the range in the absorption pattern in three main regions: (a) stretching vibration of the COO<sup>-</sup> group between 1500 and 1600 cm<sup>-1</sup>; (b) stretching vibration of the C=C group between 1600 and 1680 cm<sup>-1</sup> and (c) the C=O stretching vibration between 1690 and 1750 cm<sup>-1</sup>.

The FT-IR absorption pattern characteristic of alkenic structure was observed for all the degraded PVC samples at about 1630 cm<sup>-1</sup> (Fig. 5). It indicated that when the temperature increased, absorption by C=C would increase. Although the absorption by C=O group where wave number has been increased. The assignment of the observed band to the stretching vibration of the

C=C bonds in PVC is favored by the fact that a rather weak absorption band at  $1710\text{ cm}^{-1}$  attributed to C=O was observed for all the PVC samples (Fig. 6). The spectral range  $1690\text{-}1750\text{ cm}^{-1}$  is characteristic of absorption bands of esters, carboxylic acids and ketones, and are indicative of esterification of the polymer chain. When combined with the results from the FT-IR studies on the interaction of PVC with organic stabilizer, these results show that these materials stabilize PVC against thermal degradation by replacing labile chlorine atoms in PVC (Figs. 6 and 7).

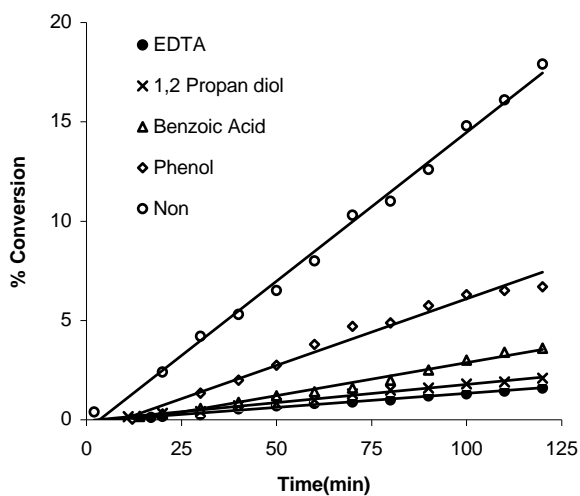


Figure 1. Dehydrochlorination of PVC (% conversion) in the presence of additives at  $180^{\circ}\text{C}$ .

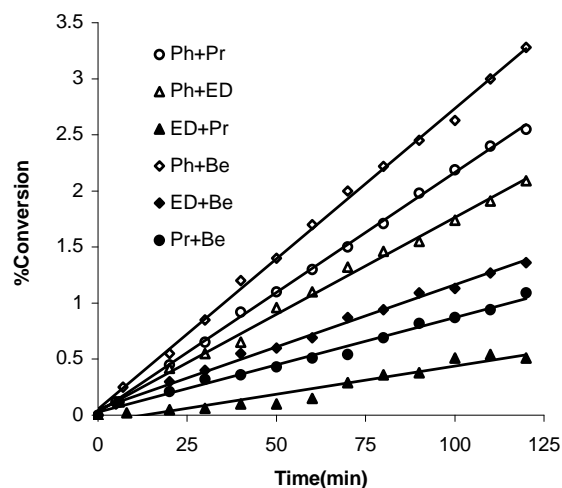


Figure 2. Effect of mixed stabilizer on the rate of dehydrochlorination of thermally degraded rigid PVC at  $180^{\circ}\text{C}$  in  $\text{N}_2$ . The overall mixed stabilizers concentration was kept at  $0.006\text{ g}/0.2\text{ g PVC}$ , Ph=Phenol, ED=EDTA, Pr=1,2 Propane diol, Be=Benzoic acid.

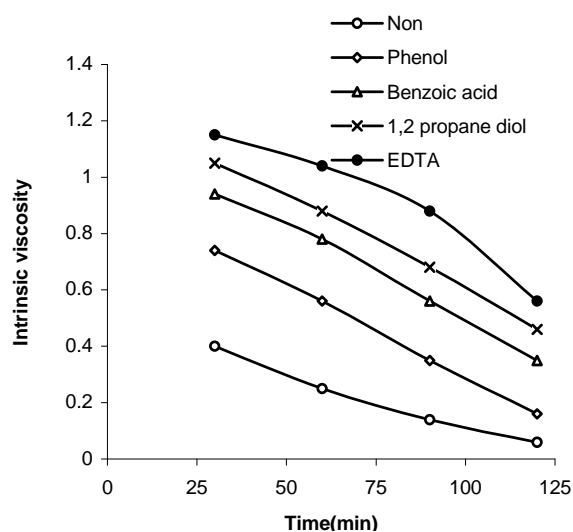


Figure 3. Intrinsic viscosity for PVC degraded in  $\text{N}_2$  at  $180^{\circ}\text{C}$ .

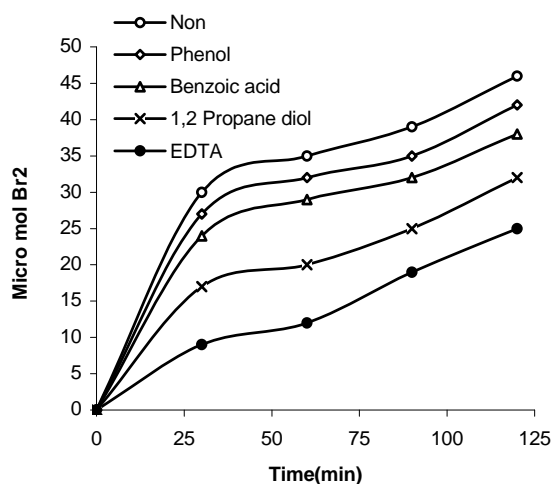


Figure 4. Bromine value consumed in the PVC degraded in  $180^{\circ}\text{C}$ .

### 3.6. The UV/Visible Absorption Spectra of PVC Samples Degraded in $\text{N}_2$ at $180^{\circ}\text{C}$ for 60 min

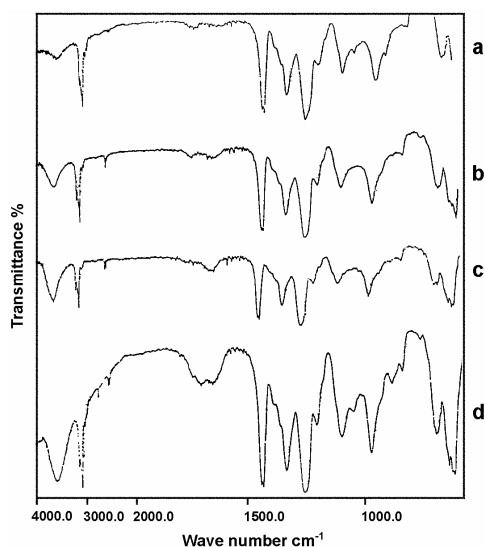
The absorption bands were characterised using the maximum wavelength values of Marks *et al.* [40]. The absorption pattern indicates that longer conjugated bond systems are present in PVC samples degraded in the absence of these materials than in the PVC samples degraded in the presence of these materials. The UV/Visible absorption spectra of PVC samples degraded in  $\text{N}_2$  are generally regarded as not providing accurate or reliable information on the level of unsaturation in the polymer, however, such spectra can

be useful in providing a basis for assessing the relative effectiveness of additives in stabilizing PVC against degradation. The results in Figure 8 show that these stabilizers exert a stabilizing effect on the thermal degradation of PVC. A second proof for the high stabilizing efficiency of the investigated stabilizers is obtained by measuring the effect of these material on the extent of discoloration of degraded PVC relative to the blank PVC. The extent of discoloration was determined colorimetrically by measuring the absorbance at  $\lambda=360$  nm for the various samples as a function of the degradation time. The results, as shown in Figure 9, reveal the lower discoloration of PVC samples stabilized by EDTA, 1,2 propane diol, benzoic acid and phenol compared with the blank.

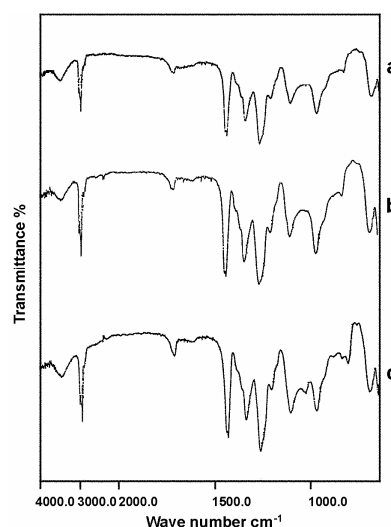
In order to propose a mechanism for stabilization by these stabilizers, we should take into account the following observations:

1- A stream of HCl gas was allowed to pass over samples of phenol or benzoic acid heated, at  $180^{\circ}\text{C}$ , in  $\text{N}_2$  for 30 min. The obtained spectrum of the product was identical to that of the untreated samples, thus these two stabilizers do not act as an HCl absorber.

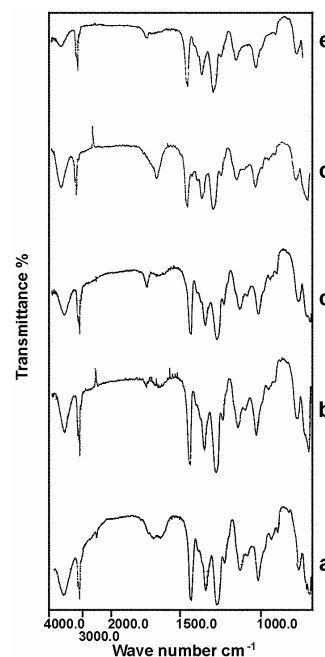
2- The two above stabilizers were dissolved in carbon tetrachloride in presence of a catalytic amount of benzophenone as photosensitizer. The solution was subjected to a low-pressure mercury lamp for 120 min. Further, the IR spectrum of the irradiated sample showed the appearance of (C-Cl) stretching vibration band at  $810\text{ cm}^{-1}$ . This indicated that two stabilizers can act as a radical trap.



**Figure 5.** Variations in the FT-IR spectra of PVC samples undegraded and degraded at  $180^{\circ}\text{C}$  in  $\text{N}_2$ , in the absence of stabilizers as a function of degradation time: (a) undegraded PVC; (b) 20 min; (c) 40 min; (d) 60 min.



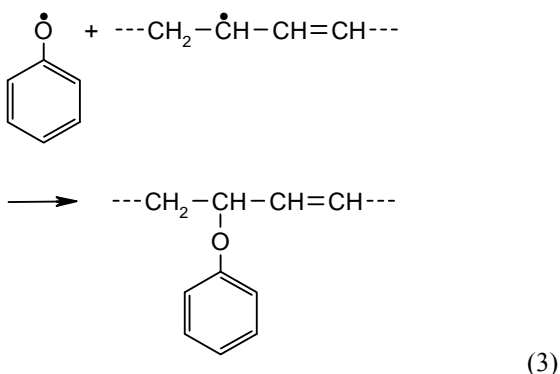
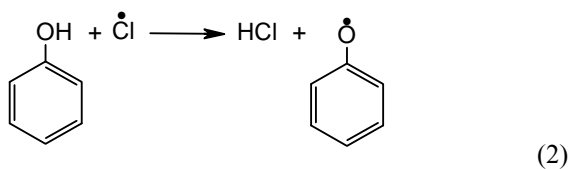
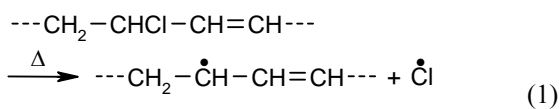
**Figure 6.** Variation in the FT-IR spectra of PVC samples degraded at  $180^{\circ}\text{C}$  in  $\text{N}_2$  in the presence of benzoic acid stabilizer as a function of degradation time: (a) 20 min; (b) 40 min; (c) 60 min.



**Figure 7.** Variation in the FT-IR spectra of PVC samples degraded at  $180^{\circ}\text{C}$  in  $\text{N}_2$  for 60 min in the presence of stabilizers: (a) non; (b) phenol; (c) benzoic acid; (d) EDTA; (e) 1,2 propane diol.

3- The polymer was found to undergo a slight cross-linking either during or after the induction period as evidenced by the partial insolubility of the degraded polymer in tetrahydrofuran. Accordingly, a probable mechanism that might account for all the aforementioned findings can be depicted as shown in Equations 1-3.

In the presence of phenol stabilizer mechanism stabilization is corresponding follow equation:



In the presence of benzoic acid stabilizer mechanism stabilization is corresponding follow equation:

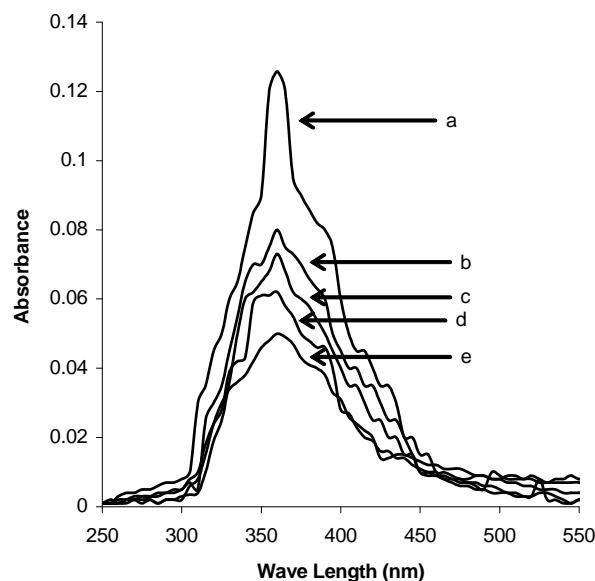
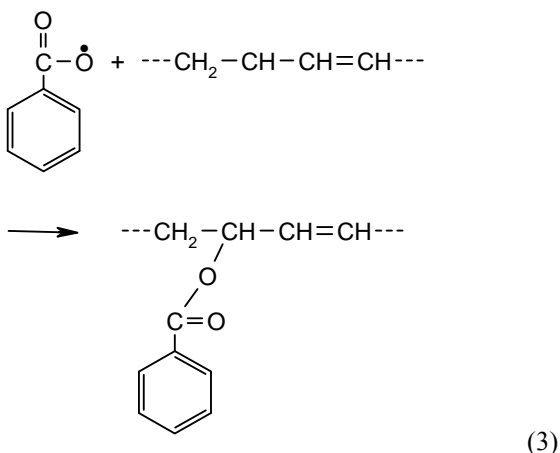
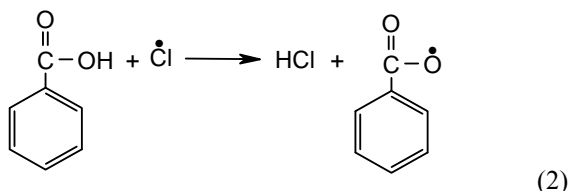
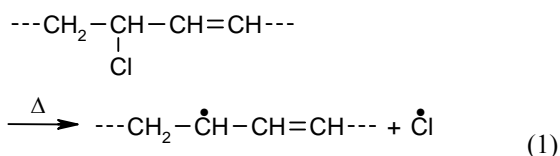


Figure 8. UV/Visible absorption spectra of PVC samples degraded in N<sub>2</sub> at 180°C for 60 min, (a) Non; (b) phenol; (c) benzoic acid; (d) 1,2 propane diol; (e) EDTA.

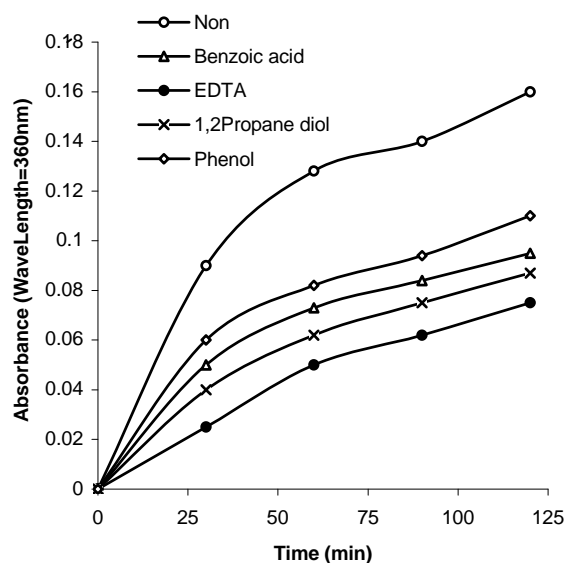


Figure 9. Absorbance-time curves for rigid PVC thermally degraded at 180°C in N<sub>2</sub> (samples concentration, 50 mg in 25 ml 1,2 dichloethane).

According to the suggested mechanism, the labile chlorine atom resulting from the initial stages of degradation (Equation 1) is directly attracted by H<sup>•</sup> radical liberated from phenol (Equation 2). Then polymer chain radical trapped by phenol that loss H (Equation 3).

Given mechanism was evidenced experimentally by following the IR spectra of the degraded stabilized PVC residue left after washing the degraded polymer thoroughly with hot ethanol, to remove the unreacted stabilizer, both during and after the induction period. Figure 6 illustrates the variation of the IR spectrum of the degraded PVC sample stabilized by benzoic acid as a function of degradation time. The presence of absorption band at 1690-1750  $\text{cm}^{-1}$  (Fig. 6) is characteristic of the aromatic moiety ( $-\text{CO}_2-$ ) that absorbance in the range increase when degradation time increase, this whiteness indicate the presence of the stabilizer moiety chemically bonded into the body of the polymeric chain [2,35].

#### 4. Conclusion

The results from this study has provided qualitative and quantitative data on the stabilizing effect of EDTA, 1,2 propane diol, benzoic acid and phenol on the thermal degradation of PVC. The stabilizing efficiency is based on measuring the length of the induction period, observed during the initial stage of degradation. The period during which no detectable amounts of HCl could be observed, and also from the rate of dehydrochlorination as measured by bromometry on one hand, and the extent of discoloration of thermally degraded PVC on the other. The results reveal the higher stabilizing efficiency of the investigated materials as thermal stabilizers for rigid PVC.

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