Stabilizing effect of epoxidized sunflower oil as a secondary stabilizer for Ca/Hg stabilized PVC

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Abstract. Unsaturated triglyceride oil sunflower was epoxidized and characterized by chemical and spectroscopic methods. Epoxidized sunflower oil (ESO) was used as an organic thermal co-stabilizer for rigid poly(vinyl chloride) (PVC) in the presence of tricalcium dicitrate ($\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$) and mercury (II) acetate ($\text{Hg}(\text{CH}_3\text{COO})_2$). The thermo-oxidative degradation of PVC was studied in the presence of these ternary stabilizer systems at 170, 180, 190 and 200°C in N_2 atmosphere. The effects of metal carboxylate combination Ca/Hg in the absence and in the presence of epoxidized sunflower oil on static heat treatment of PVC have been studied. The formation of polyene sequences was investigated by UV-visible and FT-IR spectroscopy and by comparing viscosity data obtained in the presence and in the absence of the additives. It was found that the additives retard the rate of degradation and reduce the extent of polymer chain scission associated with the thermal degradation of poly(vinyl chloride). Synergistic effects were found when stabilizer was blended in 50:50 weight ratios with either. It was found that ESO exerted a stabilizing effect on the degradation of PVC. The activation energy for degraded PVC in absence of stabilizers was $38.6 \text{ kJ}\cdot\text{mol}^{-1}$ and in the presence of Ca/Hg and Ca/Hg/ESO were 53.3 and $64.7 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.

In order of compare the efficiency of the epoxidized sunflower oil with these metal soap stabilizers, thermal stabilities were evaluated on the basis of evolved hydrogen chloride determined by conductometry technique and degree of discoloration are discussed.

Keywords: thermal properties, poly(vinyl chloride), thermal stabilization, thermo-oxidative degradation, secondary stabilizer

1. Introduction

Poly(vinyl chloride), PVC, is one of the leading thermoplastic materials. It stands second in the world after polyethylene so far as production is concerned. However, PVC shows low thermal stability [1]. It is generally accepted that poly(vinyl chloride), PVC, is an unstable polymer when exposed to high temperatures during its moldings and applications. Therefore, the poor thermal stability of PVC still remains one of its main problems [2]. Thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds [3].

Dehydrochlorination initiated at the labile site in the polymer chains. This leads to an extensive discoloration of the polymer and deterioration of its physical and mechanical properties. Possible defect structures in PVC are allylic chlorine [4], tertiary hydrogen and chlorine atom [5], end groups such as double bonds [6], oxygen containing group, peroxide residue [7], head-to-head structures [8]. Some authors have claimed that these structural irregularities are responsible and can account for the low thermal stability of PVC.

Although structural defects considerably increase the initial rate of PVC degradation, and indeed ini-

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tial rates of degradation at low conversions ($0.1 \pm 0.3\%$) have been shown to correlate well with allylic and/or tertiary chloride content of PVC [9]; it has been argued that on account of the low concentrations in normal PVC of these structural irregularities, that initiation of thermal degradation of PVC also takes place at regular monomer units [8]. In addition to the difficulties in identification and quantification of such small amount of labile allylic and tertiary chlorides within normal PVC structure, it is difficult to separate their effects on degradation from that of normal polymer units. It is now generally well accepted that random elimination of HCl from regular monomer sequence are responsible for the higher degree of conversion which degrades the polymer [10].

Because these changes are accompanied by deterioration on some of the useful properties of the polymer, it has become the practice to process PVC in the presence of heat stabilizers. Thermal stabilizers for PVC are known to function by replacing labile chlorine atoms in the polymer; they modify chain reactions and thereby inhibit the elimination of hydrogen chloride and interrupt the formation of polyene sequences in the polymer [5].

Additives that have found practical application as thermal stabilizers for PVC include metal soaps of carboxylic acids, organometallic compounds and inhibitors of radical chain reactions [9]. The most important stabilizers of PVC are different metal soaps like Pb, Cd, Ba, Ca and Zn carboxylates and some di- and mono-alkyltin compounds, e.g., maleates, carboxylates, mercaptides [11]. A wide variety of stabilizers is used industrially to improve the thermal stability of the polymer. The commonly used stabilizers are usually basic lead salts that can react with the evolved hydrogen chloride gas thus they retard the deleterious catalytic action of the eliminated hydrogen chloride, or substances that can exchange the labile functional group in the backbone chain for other more stable substituent derived from the stabilizer; for example, metallic soaps [12], esters or mercaptides of alkyl tin or material whose stabilizing action is through intervention with the radical process of degradation such as quinone tin polymer.

Moreover, the stabilizer may function by disruption of the conjugated system, thus reducing the discoloration of the polymer. Mercaptans are typical

example of these stabilizers. However, irrespective of their stabilizing efficiencies; they suffer from the deleterious effect of their byproduct, mostly metal chloride, accumulated during the reaction of these stabilizers with the polymeric chain [13].

These metal chlorides are considered as strong catalysts for the subsequent dehydrochlorination process, and they are responsible for the sudden blackening of certain formulation, and may present a serious environmental problem. This has led, recently, to the extensive use of stabilizers of an organic nature for the thermal stabilization of PVC [14].

Epoxy compounds are well known as typical non-metallic stabilizers for PVC [15]. They are generally regarded as secondary stabilizers used to enhance the effectiveness of metal soaps. They act as acceptors for the liberated hydrogen chloride [16, 17] and retardants for the appearance of discoloration [18, 19]. The effects of epoxidized sunflower (ESO) on the thermal degradation and stabilization of PVC in the presence of metal carboxylates (Ba/Cd and Ca/Zn stearates) have been investigated. ESO showed excellent properties as secondary stabilizer for PVC [20].

In this work, commercial sunflower oil was epoxidized. The stabilizing effect of epoxidized sunflower oil (ESO) on the thermal degradation of PVC in presence and absence of mixture tricalcium dicitrate and mercury (II) acetate and the ratios of Ca and Hg carboxylate (1/1, 1/2, 1/3, 2/1, 2/2, 2/3, 3/1, 3/2) and ESO in combination with Ca/Hg carboxylate under atmosphere of nitrogen have been investigated. The dehydrochlorination process in PVC degradation has been studied in detail using viscometric and spectrophotometric analysis and the values of the kinetic parameters have been calculated.

2. Experimental

2.1. Materials

Poly(vinyl chloride), PVC, suspension, with *K* value of 69–71; tricalcium dicitrate and mercury (II) acetate from Fluka 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 (60°C) [21]. Commercial sunflower oil, was used. Epoxidized sunflower oil was prepared by epoxidation. Amberlite IR-120 cross-linked ploy(styrene-sulfonic acid) ion exchange resin and hydrogen peroxide (30%) were purchased from Fluka Company. All analytical grade solvents were used as obtained from pro-labo.

2.2. Preparation of epoxidized sunflower oil (ESO)

The epoxidation of sunflower oil was carried out at 50°C using peroxy-acetic acid prepared *in situ* by reacting hydrogen peroxide (30% v/v) with excess glacial acetic acid and Amberlite IR-120 [22]. The level of epoxidation was determined using a standard analytical method [23]. ESO with oxirane oxygen level 4.5% was prepared.

2.3. Degradation of PVC: rates of dehydrochlorination

Degradation studies were carried out using PVC powder in the presence of ESO (0.04 g), tri-calcium dicitrate and mercury (II) acetate (0.008 g) at 170, 180, 190 and 200°C under nitrogen atmosphere. The PVC sample (0.5 g) was mixed thoroughly with an appropriate amount of the additive and transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 250 ml·min⁻¹. The degradation tube was then immersed in a thermostat oil bath. The amount of evolved HCl was established after various periods of time by conductometry. The extent of dehydrochlorination (conversion %) was calculated from the ratio of evolved HCl to the amount available in the polymer [24].

2.4. UV-visible analysis

UV-visible spectra of purified PVC solutions in distilled 1,2-dichloroethane (2 g/l) were obtained by using a Shimadzu 120-02 UV-visible spectrophotometer. The polymer was purified by dissolution in 1,2-dichloroethane, precipitation with methanol and filtration.

The extent of discoloration of the degradation polymer sample was measured colorimetrically at $\lambda = 360$ nm as a function of the degradation time.

2.5. FT-IR analysis

IR spectra were measured using a Shimadzu infrared spectrophotometer (FTIR-4300) in the range 600–4000 cm⁻¹ at 25°C. All the samples were mixed with KBr for these analyses.

2.6. Intrinsic viscosity measurements

The degraded PVC (0.05 g) 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. Intrinsic viscosities were determined using a setgvis kinematic from measurements in cyclohexanone solution at 30°C. The intrinsic viscosities and relative and specific viscosities of solutions were calculated by Equations (1)–(3) [25]:

$$\eta = \frac{(\eta_{sp} + 3 \ln \eta_{rel})}{4C} \quad (1)$$

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

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

where η , η_{sp} and η_{rel} are the intrinsic, specific and relative viscosities, respectively, 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 intrinsic viscosity of undegraded samples, (η/η_0), was used to deduce the effect of the additives on the degradation of PVC.

3. Results and discussion

3.1. Effect of the stabilizer concentration on the efficiency of stabilization

The results of the dehydrochlorination of rigid PVC (0.5 g) stabilized by tricalcium dicitrate in different concentrations (0.4–3% w/w) are shown in Figure 1. They indicate that with increasing of [tricalcium dicitrate]/[PVC] ratio up to about 1.6% w/w of stabilizer, the rate of dehydrochlorination decreases and thereafter it increases. It can be seen from the results that the effect of Ca on the degra-

Figure 1. Conversion [%] of rigid PVC at 180°C with 0.5 g of PVC for various concentration of tricalcium dicitrate

dation of PVC is not additive: showing antagonistic effect up to 1.6% w/w Ca and synergistic effect at higher Ca. The data of others compounds show that the stabilizing efficiency of mercury (II) acetate and ESO is greater with concentration of 1.6% w/w and 0.8% w/w, respectively. It is known that labile chlorine atoms in PVC, especially allylic and tertiary chlorine, reduce the thermal stability of this polymer [26–31].

3.2. Stabilization of thermally degraded rigid PVC using mixed stabilizer (Ca/Hg) in the absence of ESO

The results of the dehydrochlorination of thermally degraded rigid PVC (0.5 g) at 180°C in N₂ in the presence of the mixed stabilizers (Ca/Hg) are shown in Figure 2. The results clearly reveal the greater stabilizing efficiency of the mixed stabilizers, reaching its maximum when the two stabilizers were mixed in a 2:2 ratio, respectively. It can be seen that the stabilizing effect of Ca stabilizer is enhanced by the presence of Hg stabilizer. The marked reductions in the rate of dehydrochlorination using mixed stabilizer (Ca/Hg) may be attributed to synergism of Hg and Ca compounds in stabilizing PVC against thermal degradation.

The mechanism by which metal soaps stabilize PVC against thermal degradation was first proposed by Frye and Horst [32, 33] and it involves the replacement of labile chlorine atoms within PVC

Figure 2. Conversion [%] of rigid PVC at 180°C with 0.5 g of PVC containing various ratios of Ca/Hg in the absence of ESO

structure with carboxylate groups which are more stable to heat treatment.

3.3. Stabilization of thermally degraded rigid PVC using mixed stabilizer (Ca/Hg/ESO)

It is well known that the ability to prevent dehydrochlorination of PVC is an important characteristic in the evaluation of the stabilizing effect. The experimental values of dehydrochlorination of rigid PVC at 180°C in N₂ in the presence of additives and mixed additives are given in Figure 3.

Figure 3 shows the dehydrochlorination curves of PVC containing metal carboxylates and Ca/Hg (2/2) in the absence and in the presence of ESO for comparable the Ca/Hg stabilizer in the weight ratio of 1/1 when used in combination with ESO was found to be most effective.

It can be seen from Figure 3 that the lower value was obtained for the Ca/Hg (1/1)-ESO, for this synergistic mixture of stabilizers, the presence of ESO reduced effectiveness the initial rates of dehydrochlorination (DHC).

The investigated ESO exhibits a greater stabilizing efficiency compared to others. The greater stabilizing efficiency is illustrated not only by lower rates of DHC during the subsequent stages of degradation reaction, but also by the longer induction periods or the thermal stability value (T_s) during which no detectable amounts of hydrogen chloride gas are liberated and the values of the required time for dehydrochlorination to attain 1% conversion, t_{DH} , for all additives are shown in Table 1.

Table 1 gives the values of induction times and of initial rates of DHC which were computed from the slopes of the kinetic curves (Figure 3), The addition of ESO to Ca/Hg (1/1) increases the induction time and decreases the rate of DHC.

The effectiveness of ESO depends on the amount of epoxy groups in the molecule. The higher the amount of epoxy groups the better is the effectiveness. This stabilizing effect of ESO on the thermal degradation of PVC is a result of the facile reaction of HCl with epoxy groups to form chlorohydrins which is thought to reduce the autocatalytic effect of the HCl evolved. Furthermore, the esterification and etherification reactions which occur with unstable allylic chlorine groups in PVC provide an explanation for the very low values of the initial rates of DHC observed when ESO is used in combination with the Ca/Hg stearates. The observed enhanced stabilization effectiveness of the metal soaps of ESO is considered to results from the combined action of the peroxide [34].

Figure 3. Comparison of stabilizers on the rate of dehydrochlorination of degraded PVC at 180°C: (a) PVC alone, (b) PVC with 0.008 g Hg stabilizer, (c) PVC with 0.008 g Ca stabilizer, (d) PVC with 0.04 g ESO stabilizer (e) PVC with Ca/Hg stabilizers, (f) PVC with Ca/Hg/ ESO stabilizer

Table 1. Dehydrochlorination data at 180°C with 0.5 g PVC containing various stabilizers systems

Stabilizer system	T _s [min]	t _{DH} [min]	R·10 ² [conversion%/min]
none	14	38	4.8
Ca/Hg	23	53	3.3
Cu/Hg/ESO	38	71	2.4

3.4. The UV-visible absorption spectra of PVC samples degraded in N2 at 180°C

After the degradation of PVC in inert atmosphere, the resulting material was dissolved in freshly distilled 1,2-dichloroethane and UV-visible spectrum was recorded. The combination of Ca/Hg, reduced considerably the initial rates of DHC. The lower value was obtained for the Ca/Hg. For this synergetic mixture of stabilizers, UV-visible characterization of purified PVC samples treated for various times at 180°C and heated 60 min at 180°C for combination of Ca/Hg were realized. As shown in Figures 4 and 5, the combined effect would reduce the amounts of HCl evolved leading to the formation of short polyene sequences absorbing in the ultraviolet region.

Figure 4. UV-visible spectra of purified PVC stabilized with Ca/Hg (1/1) and treated for various times at 180°C

Figure 5. UV-visible spectra of purified PVC stabilized with Ca/Hg heated 60 min at 180°C

Figure 6. Absorbance-temperature curves for PVC thermally degraded at 90 min in N_2 (samples concentration, 50 mg in 25 ml 1,2-dichloroethane)

The absorption bands were characterized using the maximum wavelength values [35]. 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 N_2 are generally regarded as not providing accurate or reliable information on the level of unstauration in the polymer, however such spectra could be useful in providing a basis for assessing the relative effectiveness of stabilizers in stabilizing PVC against degradation.

A proof for the high stabilizing efficiency is obtained by measuring the extent of discoloration of degraded PVC. The extent of coloration was determined colorimetrically by measuring the absorbance at $\lambda = 360$ nm for the various samples as a function of the degradation temperatures. The results shown in Figure 6, reveal the lower discoloration of PVC samples was obtained for the Ca/Hg (1/1)-ESO.

3.5. FT-IR spectra of degraded PVC samples

In order to examine the effect of 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 and unstabilized degraded PVC and treated for various times are shown in Figure 7. In this study attention was focused on change in the absorption pattern in three main regions: (a) stretching vibration of the COO^- group between 1500 and 1600 cm^{-1} ; (b) stretching vibration of the

Figure 7. Variations in the FT-IR spectra of PVC samples undegraded and degraded at 170°C in N_2 as a function of degradation time: (a) undegraded PVC, (b) heated 30 min, (c) heated 60 min, (d) heated 90 min

C=C group between 1600 and 1680 cm^{-1} and (c) the C=O stretching vibration between 1690 and 1750 cm^{-1} .

The FT-IR absorption pattern characteristic of alkenic structure was observed for all the degraded PVC samples at about 1630 cm^{-1} . It indicated that when the temperature increases, absorption by C=C would increase, although the absorption by C=O group 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 cm^{-1} attributed to C=O was observed for all PVC samples. The spectral range 1690–1750 cm^{-1} is characteristic of absorption bands of esters, carboxylic acids and ketones, and is indicative of the esterification of the polymer chain.

FT-IR spectra of PVC alone and PVC stabilized with Ca/Hg (1/1) in the absence and in presence of ESO are presented in Figure 8.

In comparison with PVC alone, stabilized PVC samples show a band at 1560 cm^{-1} is due to the metal carboxylate which has not yet been mentioned. The band at 1730 cm^{-1} is due to oxidation products [36].

Figure 8. FT-IR spectra of (a) PVC alone, (b) PVC stabilized with Ca/Hg (1/1) and heated 90 min at 190°C, (c) PVC stabilized with Ca/Hg (1/1)-ESO and heated 90 min at 190°C

Figure 8 shows the FT-IR spectra of unstabilized PVC and PVC stabilized with Ca/Hg and PVC stabilized with Ca/Hg/ESO. The FT-IR spectra of PVC containing Ca/Hg/ESO characterized by an absorption band in the 1710–1730 cm^{-1} range. This band was absent from the spectrum of unstabilized PVC. When combined with the results from the FT-IR studies on the interaction of PVC with Ca/Hg and with Ca/Hg/ESO, these results show that these stabilizers stabilize PVC against thermal degradation by replacing labile chlorine atoms in PVC in addition to acting as HCl scavenger.

From the aforementioned observation and results, it seems reasonable to propose the following mechanism for the stabilization of thermally degraded PVC in the presence of Ca/Hg/ESO: The esterification and reactions which occur with allylic chlorine groups in PVC provide an explanation for the synergism observed in the stabilization of PVC containing a combination of an epoxy compound with metal stabilizer [37]. The mechanism of epoxidation can be displayed by Equations (4), (5) and (6)):

Epoxy compounds are well known as typical non-metallic stabilizers for PVC [20]. They are generally regarded as secondary stabilizers used to enhance the effectiveness of metal soaps. They act as acceptors for the liberated hydrogen chloride [9, 21] and retardants for the appearance of discoloration (as in Equations (7) and (8)):

3.6. Extent of thermal degradation: intrinsic viscosity

The variation in the values of relative intrinsic viscosities η/η_0 ; where η_0 is the intrinsic viscosity of undegraded polymer; and η is the intrinsic viscosity of the degraded PVC samples with degradation time are shown in Figure 9. The major types of reactions that may take place during the thermal degradation of PVC in N_2 at moderate temperature 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 under-

Figure 9. Relative intrinsic viscosity for PVC degraded in N_2 at 180°C after 90 min

going degradation decreases initially to a minimum and then increases with further increase in the number of double bonds in the polymer [38], 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 would represent the extent of degradation, the lower the values of intrinsic viscosity, the greater the extent of degradation. The results in Figure 9 show that the values of intrinsic viscosity obtained for PVC samples degraded in the presence of stabilizers are much higher than the values for unstabilized PVC samples. These results are indicative of a stabilizing effect of the materials on the thermal degradation of PVC.

3.7. Kinetics of dehydrochlorination of PVC

3.7.1. Determination of reaction order with respect of stabilizer at constant amount of PVC

The rate of reaction is determined in Equation (9):

$$R = \frac{dx}{dt} \quad (9)$$

where R is the rate of the reaction and x is the concentration of product in the reaction.

The plots of conversion % vs. $[S]$ are linear and slopes of the lines give the rate of the reaction dehydrochlorination. The rate of dehydrochlorination

depends on the concentration of stabilizer and polymer as in Equations (10) and (11):

$$R = k \cdot [\text{PVC}]^\alpha [\text{S}]^\beta \quad (10)$$

$$R = k' [\text{S}]^\beta \quad (11)$$

Experimental values of dehydrochlorination of all additives are given in Tables 2 and 3 and depicted in Figures 10, 11 and 12.

The plot of $\ln R$ vs. $\ln[S]$ is linear and for Hg, Ca and ESO stabilizers is plotted in Figure 13. The slopes of the lines give the order of the reaction with respect to stabilizers.

Figure 10. Conversion [%] of PVC at 180°C with 0.5 g of PVC for various amounts of mercury (II) acetate [g]

Figure 11. Conversion [%] of PVC at 180°C with 0.5 g of PVC for various amounts of tricalcium dicitrate [g]

Table 2. Effect of metal carboxylate amount on the rate of dehydrochlorination of PVC at 180°C with 0.5 g polymer

[S]/g	R·10 ² [conversion%/min]	
	Hg(CH ₃ COO) ₂	Ca ₃ (C ₆ H ₅ O ₇) ₂
0.002	4.7	4.5
0.004	4.4	4.3
0.006	4.1	4.2
0.008	4.0	3.9

Table 3. Effect of ESO amount on the rate of dehydrochlorination of PVC at 180°C with 0.5 g PVC

[ESO]/g	R·10 ² [conversion%/min]
0.01	0.7
0.02	4.6
0.03	4.4
0.04	4.2

Figure 12. Conversion [%] of PVC at 180°C with 0.5 g of PVC for various amounts of epoxidized sunflower oil [g]

Figure 13. $\ln R$ vs. $\ln[S]$ for mercury (II) acetate, tricalcium dicitrate and ESO stabilizer at 180°C

From the data of Tables 2 and 3 the reaction order with respect to mercury (II) acetate, tricalcium dicitrate and ESO were determined -1.05 , -1.01 and -0.05 respectively. These results show that all stabilizers are the negative orders. Thus the more negative reaction order shows that the more PVC stabilization. It is clear that $\text{Hg}(\text{CH}_3\text{COO})_2$ and $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ exhibited a greater stabilizing efficiency relative to ESO.

3.7.2. Temperature effect on the rate dehydrochlorination in degradation of PVC

The rates of degradation of PVC at various temperatures are shown in Figure 14. It can be seen that the extent of dehydrochlorination at temperatures between 170–200°C is linear.

Figure 14. Conversion [%] of PVC with 0.5 g of PVC at different temperatures

Figure 15. Conversion [%] of PVC with 0.5 g of PVC in the presence of Hg/Ca (2/2) at different temperatures

Figure 16. Conversion [%] of PVC with 0.5 g of PVC in the presence of $\text{Hg}/\text{Ca}/\text{ESO}$ (1/1/5) at different temperatures

Similar trends were observed in the degradation of PVC in the presence of mixed stabilizers 0.008 g of each metal carboxylate and 0.04 of ESO (Figures 15 and 16).

3.7.3. Calculation of activation energy

The degraded of PVC was carried out at different temperature in constant conditions (Figures 12, 13, 14). It was observed that the degradation of PVC increases with increasing temperature. The degradation rate was determined and the effect of temperature on the rate of dehydrochlorination are listed in Table 4. Then we may equalize the reaction rate to the degradation rate. Substitution of Arrhenius relation in general rate Equation (12) yields:

$$R = A [PVC]^{\alpha} [S]^{\beta} e^{-E_a / RT} \quad (12)$$

where A , E_a and T indicate collision parameter in Arrhenius equation, activation energy and absolute temperature, respectively. Other abbreviations have been defined already. In this manner, temperature is the sole variable. Recent Equation (13) may be rewritten as:

Table 4. Effect of temperature on the rate of dehydrochlorination of PVC with 0.5 g PVC

Compound	R·10 ² [conversion%/min]				<i>E_a</i> [kJ·mol ⁻¹]
	Temperature [°C]				
	170	180	190	200	
PVC	4.1	4.8	6.3	8.0	38.6
Hg/Ca/PVC	2.8	3.3	4.0	5.8	53.3
Hg/Ca/ESO/PVC	1.6	2.4	3.2	5.2	64.7

Figure 17. Plot of degradation rate upon the inverse of temperature in the absence and in the presence of mixture of stabilizers

$$\ln R = \ln k' - \frac{E_a}{RT} \quad (13)$$

where $k' = A[PVC]^{\alpha}[S]^{\beta}$. It means that if $\ln R$ versus $1/T$ [K⁻¹] values are fitted with a straight line, the activation energies of reaction, slope of plot, may be derived. The results of Table 4 are depicted in Figure 17.

The data of Table 4 show that the variation of the rates and activation energies of dehydrochlorination of PVC. The degradation rates are lower and the activation energies are higher at the presence of stabilizers, compared to the absence of stabilizer. This daringly indicates that the polymer with stabilizer is more stable than the polymer alone.

Results observed in our laboratory are consistent with other investigative works [22].

4. Conclusions

In this work, we studied degradation and stability of PVC in the absence and presence of different stabilizers at various temperatures. Epoxidized sunflower oil shows excellent properties as a secondary stabilizer for PVC when used in combination with the synergetic metal soaps (Hg/Ca).

The marked effects of ESO on the thermal stabilization of PVC could not be observed by using without the synergetic metal soaps. This ternary system retards the development of dehydrochlorination and reduces the rate of degradation. In the first case, the synergism between ESO and metal soaps results from the reduction of the initial rate of DHC due to the reaction between HCl evolved at the early stages of DHC with ESO and metal soaps which reduces its catalytic effect on the degradation of PVC as well as etherification and esterification reactions of labile chlorine atoms leading to the formation of short polymer sequences which are responsible of the absence of initial coloration. Reduction of initial rate of DHC due to the reaction between HCl evolved at the early stages of dehydrochlorination with ESO and metal soaps which reduces its catalytic effect on the degradation of PVC.

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