

Studies in the Utilization of Biobased Additives as Thermal Stabilizer for Plasticized PVC

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Abstract. Divalent metal (barium, cadmium, calcium and zinc) soaps of rubber seed oil and their binary mixtures (Ba/Cd and Ca/Zn) and epoxidized rubber seed oil (4.5% epoxide content) and its admixtures with the single divalent metal soaps were evaluated as thermal stabilizer for dioctylphthalate plasticized PVC using changes in discolouration indices (yellowness index and UV absorption at 360nm) and initial rates of dehydrochlorination measured at 140 and 160°C. The results obtained showed that the divalent metal soaps were relatively effective in stabilizing the dioctylphthalate plasticized PVC against thermal degradation and that the binary soap mixtures enhanced the heat stabilizing effectiveness: marked reduction in the values of the discolouration indices; longer dehydrochlorination induction period and smaller values of rate constant of initial rate of dehydrochlorination. It was found that epoxidized rubber seed oil was less effective in comparison with the divalent metal soaps in stabilizing plasticized PVC against thermal degradation. These results show that the bio-based additives are compatible with dioctylphthalate plasticized PVC, stable to heat within the range of temperature used in the processing of plasticized PVC, inhibit/retard dehydrochlorination and reduce the extent of degradation.

Introduction

Poly (vinyl chloride) (PVC), one of the most widely consumed plastic materials worldwide is used in unplasticized and plasticized forms in a variety of applications. About 40% of total PVC production goes into the flexible consumer products such as wire and cable insulation, flooring, wall cover and packaging materials [1]. In these applications, PVC resin is mixed with plasticizer, a low molecular weight resin or liquid, which improves the flexibility and processability of the polymer by lowering the second order transition temperature of the polymer [2]. Most flexible plastics are limited in their end-use applications because plasticizers being low-to-medium low molecular weight compounds with measurable vapour pressure below their boiling points are prone to volatilization and degradation in high temperature environments leading to tackiness and embrittlement of the plasticized materials [3]. PVC's inherent instability to heat at the molecular level is generally attributed to weak links; allylic and tertiary chloride within the polymer structure.

It has been suggested that in plasticized PVC, degradation can begin in the resin with the plasticizer being degraded thereafter or vice versa or degradation may occur simultaneously in the resin and plasticizer [4]. It is therefore important to study degradation and stabilization of PVC in plasticizer environment [5]. In the last several years, we have been engaged in the development of a range of chemical routes aimed at the utilization of rubber seed oil: in the preparation of polymers, resins and high-value additives for polymer processing [6-10]. The present paper reports on the evaluation of the stabilizing effect of derivatives of rubber seed oil (its divalent metal soaps and epoxides) on the thermal degradation of dioctylphthalate plasticized PVC.

Experimental

PVC (Petvinil P. 38/74, M_v 50,000) was used without further purification. Dioctyl phthalate (DOP) (Merck) (refractive index 1.4399 and density 0.993g/cm^3) was used as plasticizer. Epoxidized rubber seed oil (ERSO) (4.5% oxirane content) was prepared in our laboratory as described in a previous communication [11]. The barium, cadmium, calcium and zinc soaps of rubber seed oil used in this study were prepared by metathesis in aqueous alcohol as described previously [12].

Preparation of Plasticized PVC. The recipe used in the formulation of plasticized PVC samples is given in Table 1. The ingredients (PVC, DOP and additives) were mixed at room temperature to obtain a homogenous mixture. Thin films of the resulting plastisols were prepared using a $90\text{-}\mu$ film applicator and heated for 15 min in an air circulating oven at $140 \pm 2^\circ\text{C}$ to obtain plasticized films.

Table 1: Recipe for the formulation of plasticized PVC

Additives (phr PVC)	Samples							
	I	II	III	IV	V	VI	VII	VIII
DOP	80	80	80	80	80	80	80	80
Ba-RSO	3	-	-	-	-	-	3	-
Cd-RSO	-	3	-	-	-	-	-	3
Ca-RSO	-	-	3	-	-	-	-	-
Zn-RSO	-	-	-	3	-	-	-	-
ERSO	-	-	-	-	-	3	3	3

Thermal stabilization studies. The effect of the rubber seed oil derivatives on the thermal stability of the DOP-plasticized PVC was examined by measurement of discolouration indices (Yellowness Index and number of polyene sequences with six conjugated double bonds, 6-ens) and initial rates of dehydrochlorination.

Static oven heat stability tests. The plastigel samples were degraded at 160°C in an air-circulating oven for 30 min and were thereafter subjected to Yellowness Index measurement using the UNE 53-387-86 standard procedure [13] and UV absorbance measurement at 360nm using a Perkin-Elmer Lambda 45 UV spectrophotometer. Changes in Yellowness Index (YI) and in the number of conjugated double bonds associated with the degradation procedure were used to assess the effect of the additives on the thermal degradation of the plasticized PVC samples.

Thermal dehydrochlorination studies. The rates of dehydrochlorination of the plasticized PVC samples containing the rubber seed oil derivatives were measured under nitrogen atmosphere at 140 and 160°C using the 763 PVC Thermomat equipment. A detailed description of the equipment and

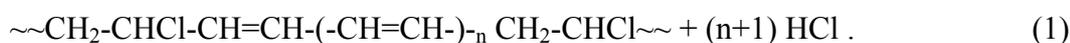
its use in dehydrochlorination studies were given previously [14]. The rate of dehydrochlorination was monitored by measuring changes in the conductivity of deionized water into which the products of PVC degradation were passed as a function of time. Dehydrochlorination was characterized in terms of induction time (a period of time in which there is no apparent change in the measured conductivity), stability time (time for conductivity to reach $50\mu\text{Scm}^{-1}$) and initial rate constant of dehydrochlorination using the procedure described by Atakul *et al* [14].

Results and Discussion

Thermal degradation of PVC at low to moderate temperatures is characterized at the initial stages of degradation mainly by the loss of HCl molecules (dehydrochlorination) which leads to the formation of conjugated double bonds and discolouration of the polymer.



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It has therefore become a common practice to evaluate stabilizers on the basis of their effectiveness in preventing discolouration of PVC at elevated temperatures. The common indices of discolouration are Yellowness Index (YI) and number of polyene sequences with six conjugated double bonds (6-ens) in degraded PVC. At low to moderate temperatures, HCl is the only volatile product of PVC degradation; therefore measurement of the rate of HCl loss and the determination of kinetic parameters of dehydrochlorination at the initial stages of PVC degradation also provide a sensitive method for assessing the effect of additives on the degradation process.

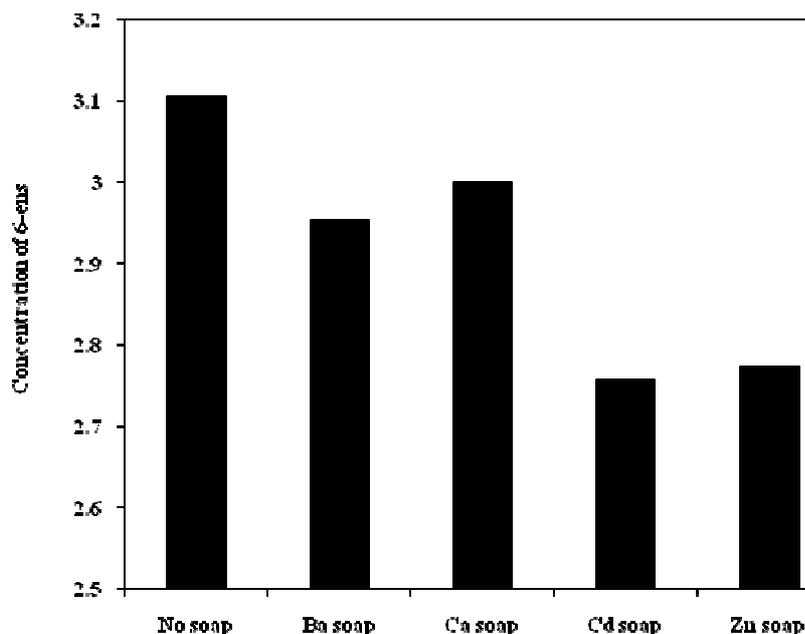
Stabilizing effect of metal soaps of RSO

Discolouration indices. The changes in the colour of plasticized PVC processed at 140°C and then heated at 160°C are given in Table 2.

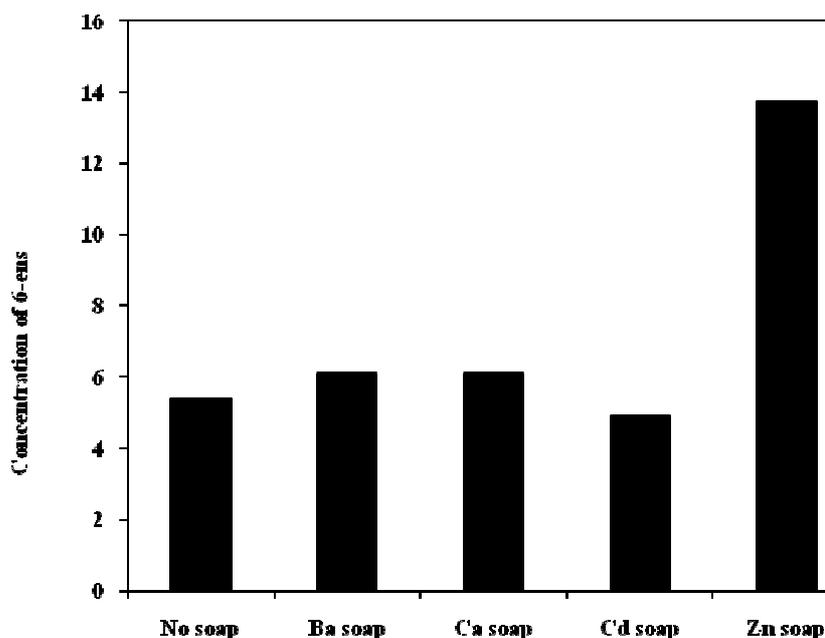
Table 2. Colour and Yellowness Index of plasticized PVC samples

Additive	Yellowness Index		Colour	
	Undegraded	Degraded	Undegraded	Degraded
None	4.23	33.95	White	Light brown
Ba-RSO	12.69	35.39	Yellow	Yellow
Ca-RSO	9.09	35.01	Light Yellow	Brown
Cd-RSO	4.01	27.36	Light Yellow	Yellowish brown
Zn-RSO	8.19	51.34	Light Yellow	Dark Yellow

The colour of the plasticized PVC samples before heating at 160°C (thermal degradation test) was generally light yellow, except for the sample containing Ba-RSO which showed a deeper hue of yellow; and values of YI ranging from about 17 for the unstabilized PVC to 37 for the sample containing Ba-RSO were obtained. Changes in the values of YI of the plasticized PVC samples after thermal degradation showed that the unstabilized plastigel gave higher values of increase in YI than for samples containing soaps of RSO, suggesting that the soaps of RSO reduce discolouration during PVC degradation. The concentration of 6-ens measured at 360nm of degraded plasticized PVC samples is shown in Fig. 1. These results show that the soaps of RSO, with the exception of Zn-RSO have no marked effect on discolouration during PVC degradation.



(A)



(B)

Figure I. Concentration of 6-ens (A) Plasticized PVC (B) Plasticized PVC heated for 30min at 160°C

Dehydrochlorination kinetics of plasticized PVC. Thermal dehydrochlorination studies on the PVC plastigels were carried out at 140 and 160°C under nitrogen by measuring changes in the conductivity of deionized water into which the HCl evolved from the samples were passed. Figure II shows the changes in the conductivity measured as a function for the samples degraded at 160°C. Similar plots were obtained at 140°C.

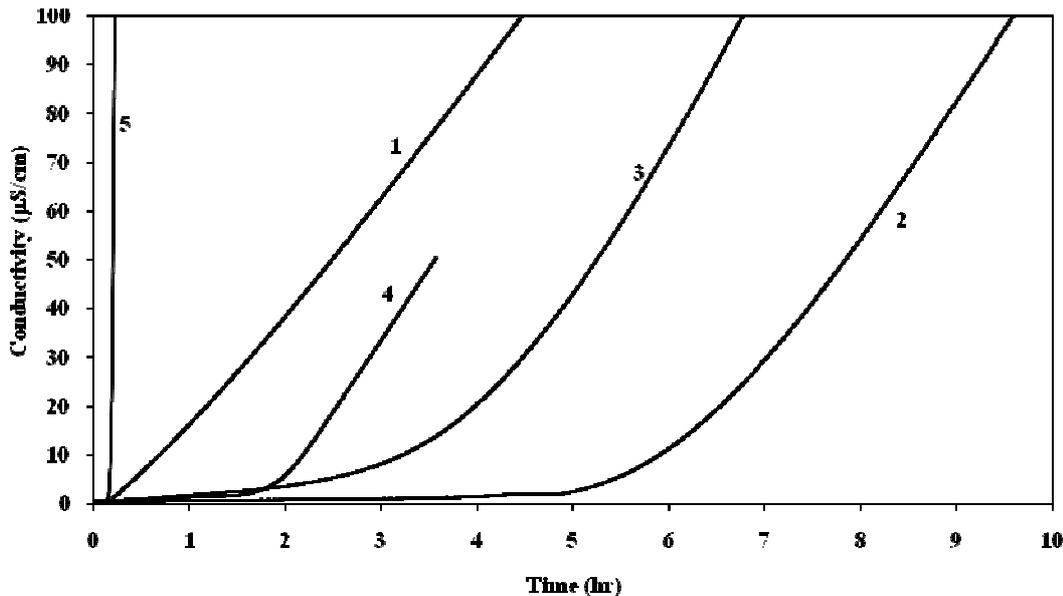


Figure II. The change of conductivity of aqueous solution with respect to time at 160°C for plasticized PVC stabilized with metal soaps of RSO. (1) None (2) Ba-RSO (3) Ca-RSO (4) Cd-RSO (5) Zn-RSO

It can be seen that the rate of dehydrochlorination can be divided into two sections: an initial low rate of HCl evolution preceding the induction period, followed by a region of more rapid dehydrochlorination. The induction period and stability time deduced from the plots are given in Table 3. Also given in Table 3 are the values of the rate constants of dehydrochlorination; k_i , corresponding to the initial portions of the plots.

Table 3. Thermal stabilization parameters of plasticized PVC samples degraded at 140°C

Additive	Induction time (hr)	Stability time (hr)	$10^6 k_i$ (min^{-1})
None	5.06; 0.74 ^a	16.13; 3.37 ^a	1.44; 2.56 ^a
Ba-RSO	27.00; 4.99 ^a	31.33; 7.86 ^a	1.67; 4.15 ^a
Ca-RSO	15.20; 3.74 ^a	17.92; 5.26 ^a	1.94; 10.10 ^a
Cd-RSO	12.00; 2.00 ^a	16.69; 3.57 ^a	2.35; 11.60 ^a
Zn-RSO	7.00; 3.22 ^a	8.66; 3.87 ^a	13.30; 5.26 ^a

^a = values obtained for plasticized PVC samples degraded at 160°C

These results show that in the presence of soaps of RSO, the plasticized PVC exhibited longer induction and stability periods than the unstabilized samples indicating retardation and inhibition of dehydrochlorination. The value of the rate constants of dehydrochlorination of the PVC plastigels would seem to suggest that the soaps of RSO accentuate the rate of dehydrochlorination. It is pertinent to mention that the nature of the plots of conductivity versus time precluded the determination of the rate constants at the same extent of degradation for all the samples. Therefore the values of k_i while not providing a reliable basis for evaluating kinetic parameters relevant to the effect of the soaps of RSO on the thermal degradation of plasticized PVC, it provides an overall assessment of the relative effect of the additives on the process of dehydrochlorination: Zn-RSO being the least effective and Ba-RSO the most effective of the soaps of RSO studied in retarding/inhibiting thermal dehydrochlorination of the plasticized polymer.

The effect of binary soap mixtures; Ba/Cd and Ca/Zn on the dehydrochlorination of plasticized PVC was studied at 160°C. Figures III and IV show typical plots of the variation of conductivity with time for PVC stabilized with Ba/Cd and Ca/Zn soap mixtures respectively.

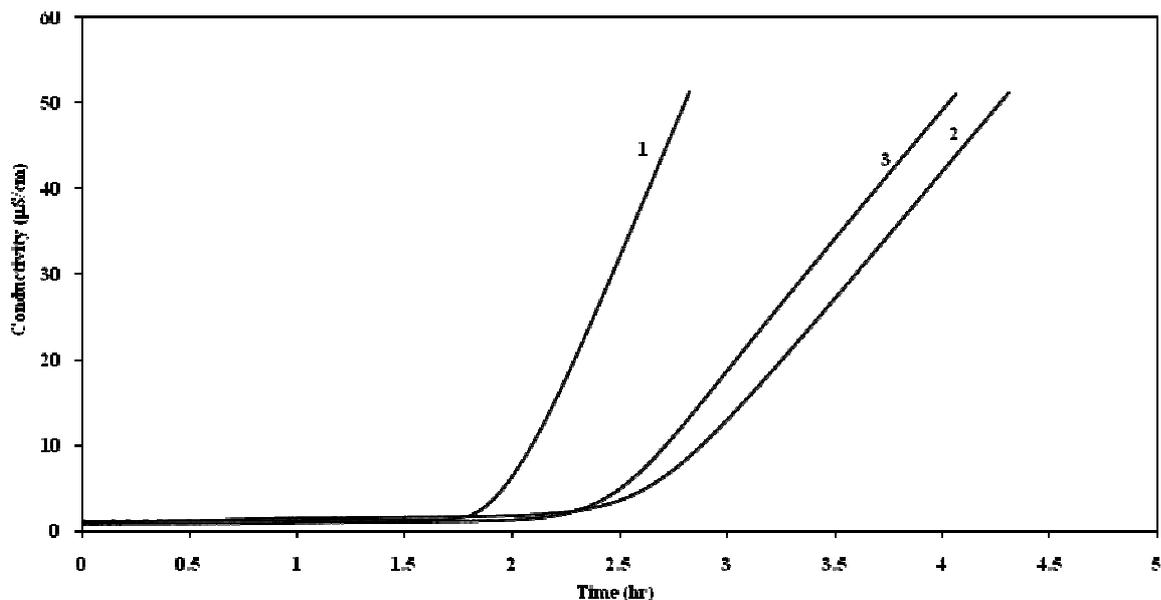


Figure III. The change of conductivity of aqueous solution with respect to time at 160°C for plasticized PVC stabilized with metal soaps of RSO. (1) 10% Cd soap (2) 50% Cd soap (3) 90% Cd soap.

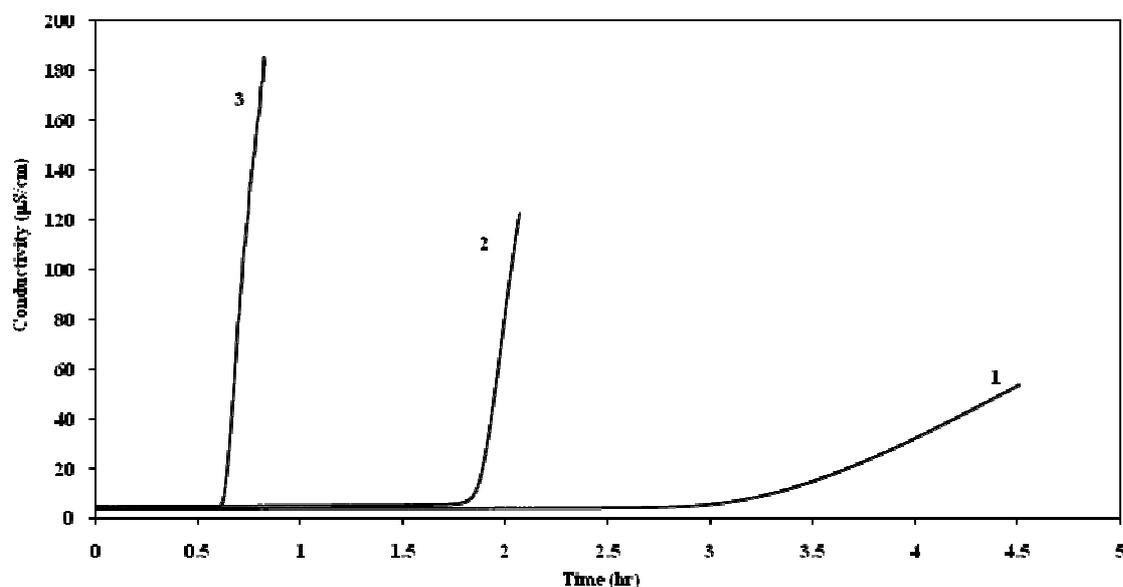


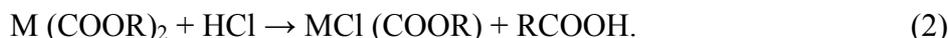
Figure IV. The change of conductivity of aqueous solution with respect to time at 160°C for plasticized PVC stabilized with metal soaps of RSO. (1) 10% Zn soap (2) 50% Zn soap (3) 90% Zn soap.

The kinetic parameters: induction time, stability time and initial rate constants of dehydrochlorination are given in Table 4.

Table 4. Kinetic parameters for the degradation of plasticized PVC stabilized with ERSO and ERSO/metal soap mixtures

Additive	Induction time (hr)	Stability time (hr)	$10^6 k_i$ (min ⁻¹)
Ba/Cd soap mixtures:			
(% Cd-RSO)			
0	2.73	5.08	2.82
10	1.87	2.82	3.41
50	2.64	4.31	3.79
90	2.50	4.06	2.00
100	3.07	4.18	3.98
Ca/Zn soap mixtures:			
(% Zn-RSO)			
0	2.44	4.41	2.48
10	3.12	4.51	5.36
50	1.88	1.96	32.60
90	0.62	0.68	85.30
100	1.02	1.08	48.80

The results in Table 4 show that the soap mixtures are relatively more effective than the single soaps (particularly the covalent metal soaps; Cd-RSO and Zn-RSO) in stabilizing the plasticized PVC against thermal degradation. This observed enhanced stabilizing is thought to result from the reaction between the more reactive covalent metal soap with the HCl evolved at the initial stages of dehydrochlorination to form the chlorinated metal soap:



which accumulates during the induction period, and thereafter decomposes to form the metal chloride [15]



The enhanced stabilizing effect is thought to result from the exchange reaction between the unreacted alkali metal soap (Ba-RSO and Ca-RSO) and the metal chloride; a reaction that precludes the deleterious effect of the latter on the degradation process



Stabilizing effect of ERSO and ERSO/metal soap mixtures

Discolouration indices. Table 5 shows that the extent of discolouration as measured by Yellowness Index is lower by up to 10 YI units in the plasticized PVC samples containing the additives of RSO (ERSO and metal soaps of RSO) than in the sample without the additive. Figure V shows that the number of polyene sequence with six conjugated double bonds (6-ens) in the degraded PVC samples is smaller for samples containing RSO additives (except for the sample containing ERSO + Cd soap) than the unstabilized sample. The relative stabilizing effect is of the order ERSO ≤ ERSO + Ba soap < ERSO + Cd soap.

Table V. Colour and Yellowness Index of plasticized PVC. Effect of rubber seed oil derivatives

Additive	Yellowness Index		Colour	
	Undegraded	Degraded	Undegraded	Degraded
None	4.23	33.95	White	Light brown
ERSO	3.73	28.42	White	Light yellow
ERSO + Ba soap	3.14	28.60	Light Yellow	Yellow
ERSO + Cd soap	6.24	24.03	White	Light yellow

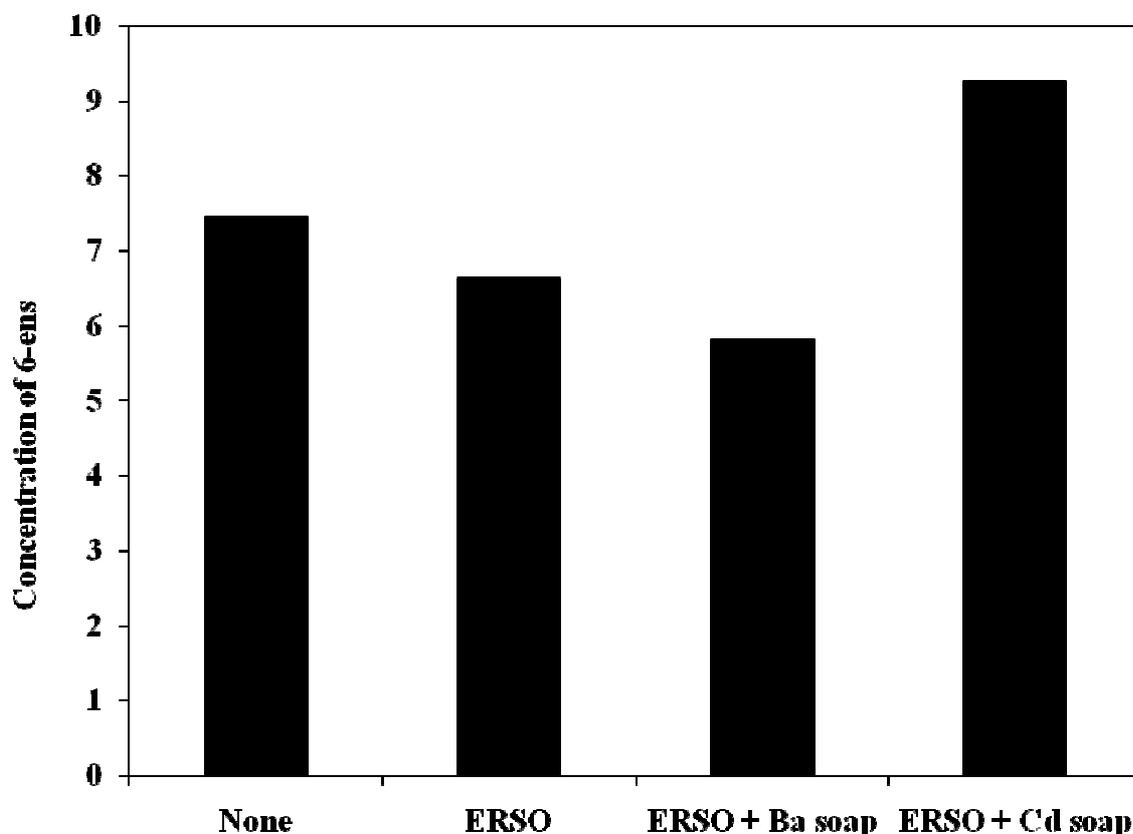


Figure V. Concentration of 6-ens for unstabilized and stabilized PVC samples with metal soaps of RSO and ERSO after degradation at 160°C for 30 mins.

Dehydrochlorination studies. The effect of ERSO and soaps of RSO on the thermal dehydrochlorination of plasticized PVC at 160°C are shown in Figure VI. Similar plots were obtained at 140°C. The induction and stability period that characterized the dehydrochlorination process of the plasticized PVC samples are given in Table 6. The results in Table 6 show that the addition of the RSO additives to plasticized PVC is associated with marked increase in induction and stability time in comparison with the unstabilized plastigel and provide clear indication of stabilizing effect of ERSO/metal soap of RSO. The relative heat stabilizing effectiveness of the additives based on the measured parameters of dehydrochlorination is of the order ERSO + Ba soap > ERSO + Cd soap > ERSO and is consistent with the results obtained from discolouration measurement (Yellowness Index).

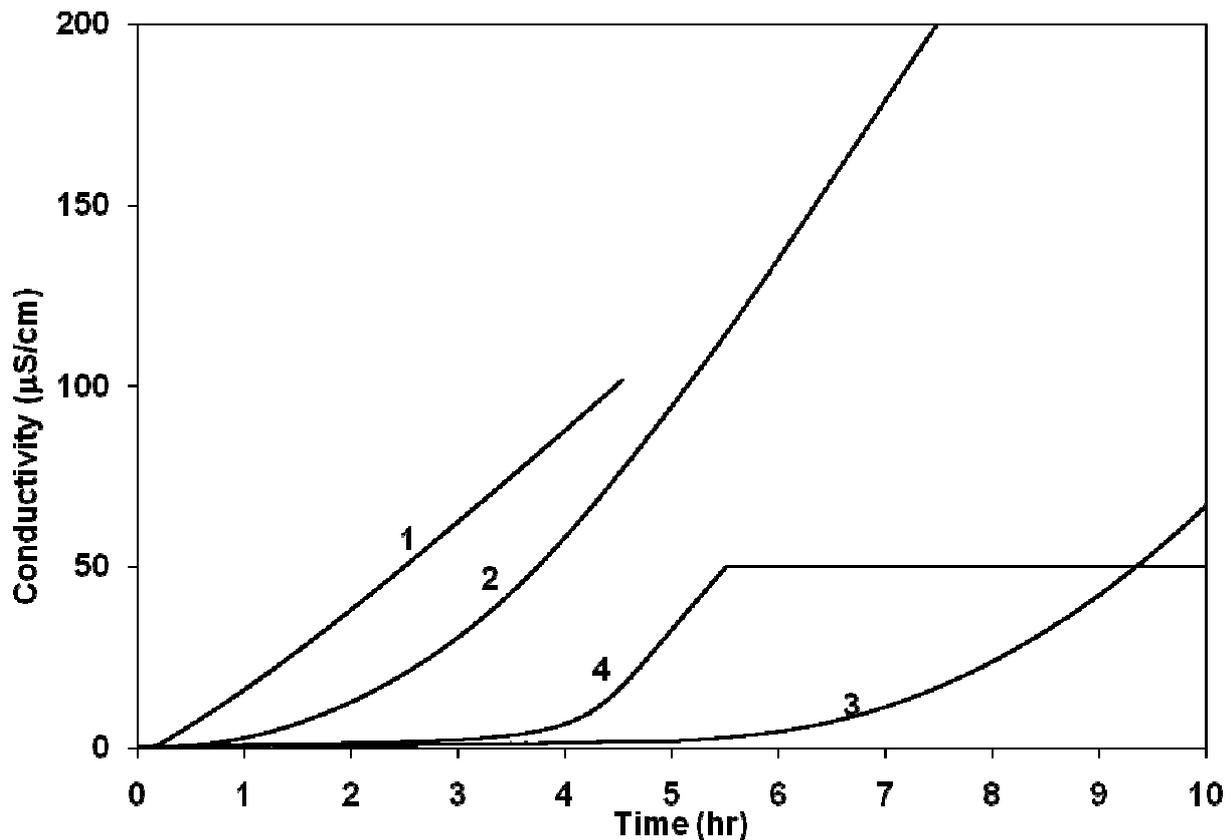


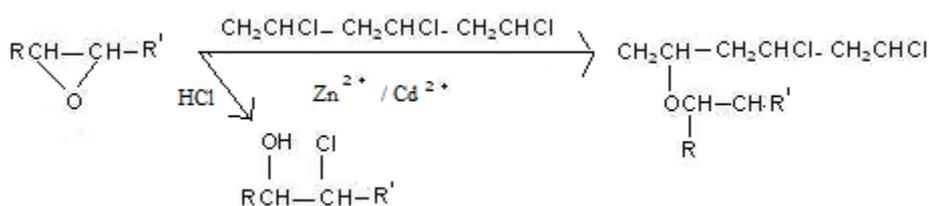
Figure VI. The change of conductivity of aqueous solution with respect to time at 160°C for plasticized PVC stabilized with metal soaps of RSO. (1) None (2) ERSO (3) ERSO + Ba soap (4) ERSO + Cd soap.

Table 6. Effect of ERSO and soaps of RSO on the thermal dehydrochlorination of plasticized PVC at 160°C

Additive	Induction time (hr)	Stability time (hr)
ERSO	1.71 (8.20)	5.06 (21.90)
ERSO + Ba soap	8.00 (31.00)	9.35 (35.10)
ERSO + Cd soap	4.30 (19.50)	5.51 (23.00)
None	0.74 (5.06)	3.37 (16.13)

Values in parenthesis are for dehydrochlorination at 140°C

The enhanced stabilizing effect of the admixtures of ERSO and metal soaps can be attributed to the combined effect of the epoxy group and the metal soap on the degradation process. Epoxy compounds are not only able to bind HCl but can also substitute labile chlorine atoms in PVC under the catalytic influence of the metal ions.



(5)

Metal carboxylates are also known to replace labile chlorine atoms within PVC with more heat stable soap moiety. The first evidence for this reaction was provided from the work of Frye and Horst [16]. These combined reactions of scavenging the HCl evolved at the early stages of degradation (which precludes its autocatalytic effect on the degradation process) and the replacement of labile chlorine atoms with more heat stable moieties of the soap and epoxide (which retard dehydrochlorination) explain the enhanced stabilizing effect of the admixtures of ERSO and the metal soaps of RSO on the thermal degradation of the plasticized PVC.

Conclusion

The effect of some divalent metal soaps of RSO, their admixtures, epoxidized RSO and its admixtures with the divalent metal soaps of RSO on the thermal degradation of plasticized PVC was studied. The observed stabilizing effect indicate a potential for the technical application of RSO in the preparation of additives suitable for use in the processing of vinyl polymers.

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