

# Thermal Dehydrochlorination of Poly(vinyl chloride) in the Presence of Jatropha Seed Oil

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## SYNOPSIS

Thermal degradation of poly(vinyl chloride) was studied in a nitrogen atmosphere in the presence of Jatropha seed oil, epoxidized Jatropha seed oil, and soaps (barium and cadmium) of Jatropha seed oil at various temperatures. The rate of dehydrochlorination measurement at 1% degradation,  $R_{DH}$ , and the time required for dehydrochlorination to attain 1% conversion were used to assess the effect of the additives on the susceptibility of the polymer to dehydrochlorination. It was found from the kinetic studies and the results from viscosity measurements on degraded polymer samples that the Jatropha seed oil derivatives suppressed the initial loss of HCl from the polymer and the extent of polymer chain scission accompanying the dehydrochlorination process. Thermal degradation studies of poly(vinyl chloride) in the presence of mixtures of barium and cadmium soaps of Jatropha seed oil were also carried out. It was found that soap mixtures containing less than 80 wt % cadmium soap exerted a deleterious (antagonistic) effect on the degradation of poly(vinyl chloride) while in the presence of soaps containing more than 80 wt % cadmium soap, considerably lower values of  $R_{DH}$  and higher values of  $t_{DH}$  were observed. The soap mixture containing 90 wt % cadmium soap was found to exhibit a remarkably improved stabilizing effect on the dehydrochlorination of poly(vinyl chloride). © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The low thermal stability of poly(vinyl chloride) (PVC) is one of the inherent problems associated with the manufacture and use of a polymer. At elevated temperature, well below its decomposition temperature, PVC loses HCl and becomes discolored, leading to a deterioration of properties. Thermal degradation of PVC is generally considered to be initiated at unstable sites within the structure of the polymer. Excellent reviews of the nature of these structural abnormalities and their deleterious effect on the thermal stability of PVC have been published.<sup>1-3</sup> The poor thermal stability of PVC requires the use of stabilizers in the processing of the polymer. Several workers<sup>4-12</sup> reported on the degradation and stabilization of PVC. Thermal stabilizers for PVC are known to function by replacing labile atoms in the polymer; they modify chain reactions and

thereby inhibit the elimination of HCl and interrupt the formation of polyene sequences in the polymer. 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.

In our previous studies, we reported on the suitability of rubber seed oil (RSO) in the preparation of alkyd resins<sup>13-15</sup> and on the stabilizing effects of derivatives of RSO on the thermal degradation of PVC.<sup>16-19</sup> The results obtained from the latter studies required that other locally nonedible, readily available vegetable oils be investigated. The overall purpose of these studies is to develop value-added products from local resources. In the present study, we report on the effect of Jatropha seed oil (JSO) and some of its derivatives on the thermal degradation of PVC.

Jatropha seed oil (JSO) is obtained from the seeds of the plant *Jatropha multifida*. *J. multifida* is a medium-sized woody plant with simple palmate or lobed leaves and umbel inflorescence. The plant has a brightly colored flower, which makes it an orna-

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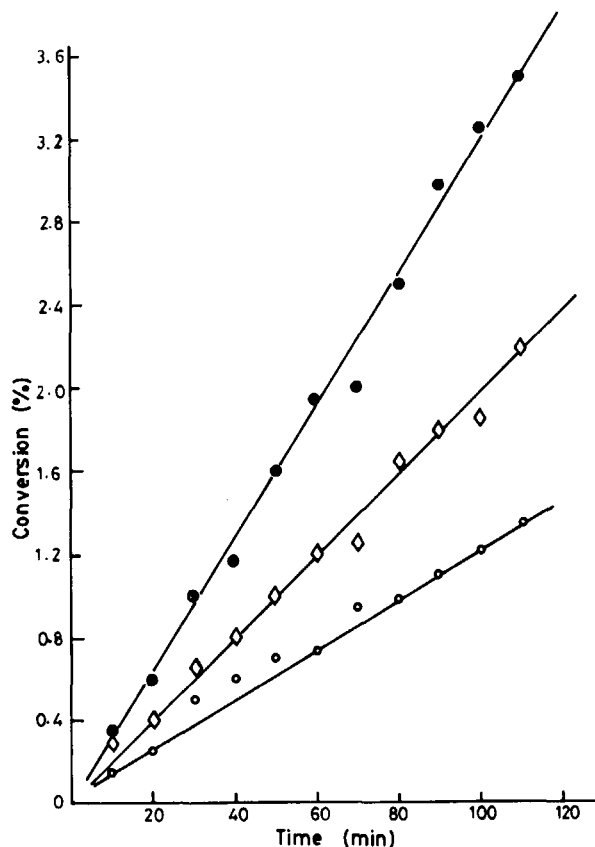


Figure 1 Dehydrochlorination of PVC at (●) 190°C, (◇) 180°C, and (○) 170°C.

mental plant. The fruit tends to be capsular: green when tender, yellow when strong, and dark brown when dry. The dried fruits consist of three seeds which are wind-dispersed. The plant exudes a whitish sap which is used locally for the treatment of sore gums (pyorrhea).

JSO has the following characteristics: specific gravity 0.91, iodine value 157.36, refractive index 1.48, acid value 5.61, free fatty acid 2.70, and boiling point 96–97°C.

## EXPERIMENTAL

### Materials

PVC (BDH) ( $\bar{M}_n$   $1.0 \times 10^5$ , particle size of 100% passes B.S 60 mesh and 74% passed B.S 200 mesh) was purified by solution in THF/acetone 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. JSO was extracted with *n*-hexane from *Jatropha* seeds collected from within Benin City.

### Epoxidation of *Jatropha* Seed Oil

Epoxidation of JSO was carried out at 29°C using peracetic acid prepared *in situ* by reacting various amounts of hydrogen peroxide (30% v/v) with excess glacial acetic acid. The level of epoxidation of JSO was determined using the method described by Durbetaki.<sup>20</sup> The boiling points of both JSO and epoxidized JSO (EJSO) were determined. The EJSO samples were stored at 7°C until required.

### Preparation of Soap from *Jatropha* Seed Oil

Metal soaps were prepared from JSO using the method described by Burrows et al.<sup>21</sup> The oil (9.2 g) was dissolved in 50 mL of hot ethanol and then treated with 20 mL of 20% (w/v) NaOH solution. To this mixture, 100 mL of 30% (w/v) solution of the metal salt were slowly added with continuous stirring. The precipitated soap was filtered off, washed with hot water, and air-dried. The soaps were prepared using  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cd}(\text{NO}_3) \cdot 4\text{H}_2\text{O}$ .

### Dehydrochlorination

Dehydrochlorination studies were carried out using PVC powder in the presence of 10 wt % JSO and EJSO between 170 and 190°C. The detailed experimental procedure was as described previously.<sup>19</sup> The

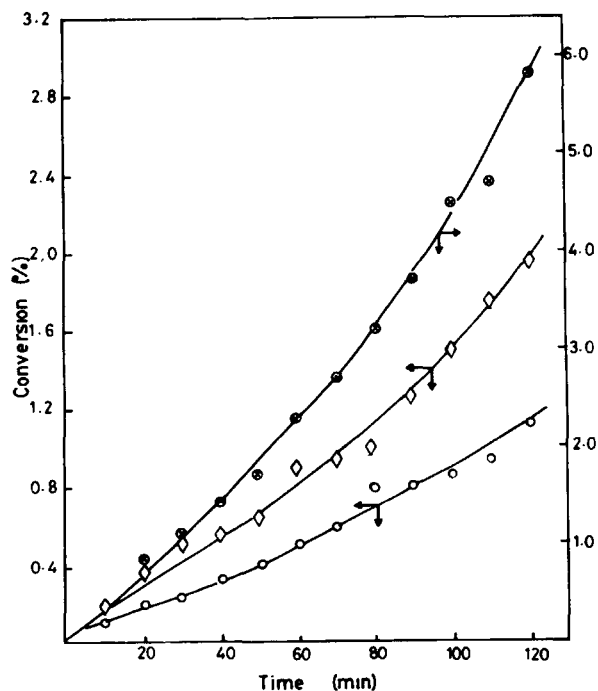


Figure 2 Dehydrochlorination of PVC in the presence of JSO at (●) 190°C, (◇) 180°C, and (○) 170°C.

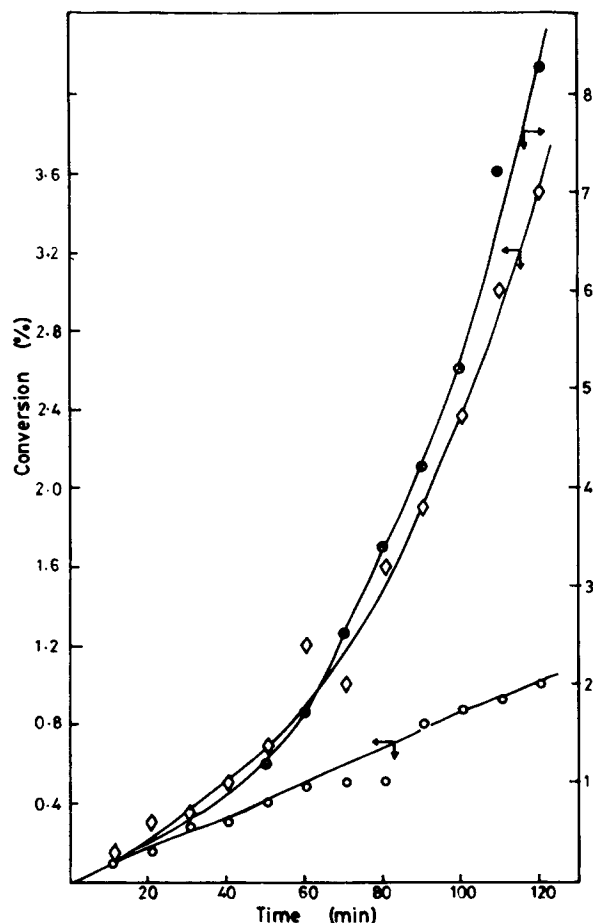


Figure 3 Dehydrochlorination of PVC in the presence of 1 mol % EJSO at (●) 190°C, (◇) 180°C, and (○) 170°C.

polymer sample (1.5 g) was mixed thoroughly with the appropriate amount of the additive and transferred to a degradation tube. The tube was connected to a source of dry nitrogen maintained at a flow rate of 60 cm<sup>3</sup>/min. The degradation tube was then immersed in a thermostat oil bath. 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 the HCl evolved to the amount available in the polymer.

#### Intrinsic Viscosity Measurements

Thermal degradation of PVC was carried out for various intervals of time (30, 60, and 90 min) in a nitrogen atmosphere. After degradation, the tube was cooled and the contents were dissolved in cyclohexanone. The cyclohexanone solution was poured into methanol with constant stirring. The precipitated PVC was filtered off and washed several times with methanol, dried in a vacuum at room

temperature, and stored in the dark. Intrinsic viscosities were determined from measurements in the cyclohexanone solution at 30°C.

## RESULTS AND DISCUSSION

The rates of dehydrochlorination of PVC at 170, 180, and 190°C in the absence of any additive are shown in Figure 1. The times required for degradation to attain 1% conversion,  $t_{DH}$ , were found to be 82, 50, and 31 min at 170, 180, and 190°C, respectively, while the rates of degradation were determined to be 0.009, 0.0167, and 0.0286% min<sup>-1</sup>, respectively.

The rates of dehydrochlorination of PVC in the presence of JSO at 170, 180, and 190°C are shown in Figure 2. It can be seen that although no initial induction periods are observed the rate of evolutions of HCl was initially relatively slow and gradually increased, attaining a steady rate after about 40 min. It has been suggested that the time required for the evolution of HCl to attain a steady rate provides an

Table I Dehydrochlorination Data of PVC in the Presence of Jatropha Seed Oil (JSO)

Additive	Temp (°C)	10 <sup>2</sup> $R_{DH}$ (% min <sup>-1</sup> )	$t_{DH}$ (min)	
None	170	0.90	82	
	180	1.67	50	
	190	2.86	31	
JSO (10 wt %)	170	0.83	119	
	180	1.33	75	
	190	3.70	27	
EJSO (10 wt %)	1 mol % epoxidized	170	1.0	120
		180	2.86	63
		190	3.30	45
	5.6 mol % epoxidized	170	1.25	100
		180	2.00	70
		190	4.00	32
	9.5 mol % epoxidized	170	2.50	92
		180	3.30	78
		190	6.60	39
Metal soaps from JSO (3 wt %)	Barium soap	180	1.60	87
		190	2.00	59
	Cadmium soap	180	1.33	120
		190	1.82	74

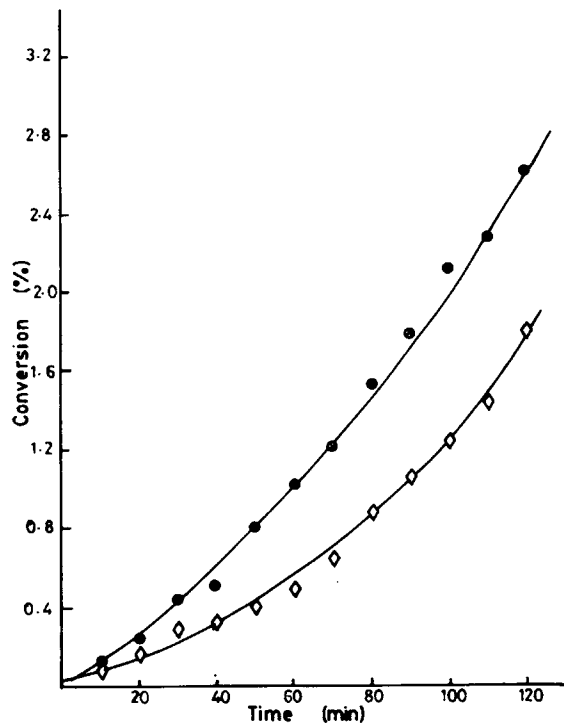


Figure 4 Dehydrochlorination of PVC in the presence of barium soap of JSO at (⊗) 190°C and (◇) 180°C.

estimate of the induction period.<sup>22</sup> The rates at 1% degradation were of the same order of magnitude ( $10^{-2} \% \text{ min}^{-1}$ ). The values of  $t_{\text{DH}}$  ranged from 27 min at 190°C to 119 min at 170°C. When compared with the values obtained for degradation in the absence of JSO, these results indicate that JSO exerts some stabilizing effect on the degradation of PVC except at 190°C, where the values of  $R_{\text{DH}}$  and  $t_{\text{DH}}$  suggest a deleterious effect. It is thought that a breakdown of some components of JSO may lead to products which accentuate dehydrochlorination. A similar trend was reported for the degradation of PVC in the presence of rubber seed.<sup>19</sup>

Figure 3 shows the rates of dehydrochlorination of PVC in the presence of 10 wt % epoxidized (1 mol %) JSO at 170, 180, and 190°C. Similar results were obtained using 5.6 and 9.5 mol % EJSO. The values of  $R_{\text{DH}}$  and  $t_{\text{DH}}$  obtained for the degradation of PVC in the presence of these additives are shown in Table I. The results show that in the presence of EJSO dehydrochlorination of PVC is accentuated and that the deleterious influence depends on the extent of epoxidation.

It was thought that the facile reaction of the epoxide with HCl evolved at the early stages of degradation would reduce the catalytic effect of HCl on dehydrochlorination and should reduce the rate of dehydrochlorination. It was found that the boiling

point of JSO was reduced by epoxidation. Whereas the boiling point of JSO was about 97°C, the value for EJSO ranged from 94°C to 80°C for 1 and 9.5 mol % EJSO, respectively. The relatively low stability of EJSO at the degradation temperatures would compromise its reactivity with HCl with implications of its ability to suppress the catalytic effect of HCl on the dehydrochlorination process.

The rates of dehydrochlorination of PVC in the presence of barium soap of JSO are shown in Figure 4. Similar results were obtained using cadmium soap of JSO. The values of  $R_{\text{DH}}$  and  $t_{\text{DH}}$  (Table I) show that the metal soaps from JSO are more effective than are EJSO and JSO in suppressing dehydrochlorination of PVC, with the cadmium soap of JSO tending to be more effective in the stabilization of PVC. The use of metal soaps of organic acid as a stabilizer for PVC relies on their ability to interact with the HCl evolved in the early stages of dehydrochlorination. It is also expected that an additive used as a thermal stabilizer should be stable at the processing temperature of the polymer. The relatively greater effectiveness of the metal soaps from JSO in stabilizing PVC against degradation than that of EJSO and JSO may be as a result of the higher stability of the soaps (mp between 120 and 156°C) than that of both EJSO and JSO at the degradation temperatures.

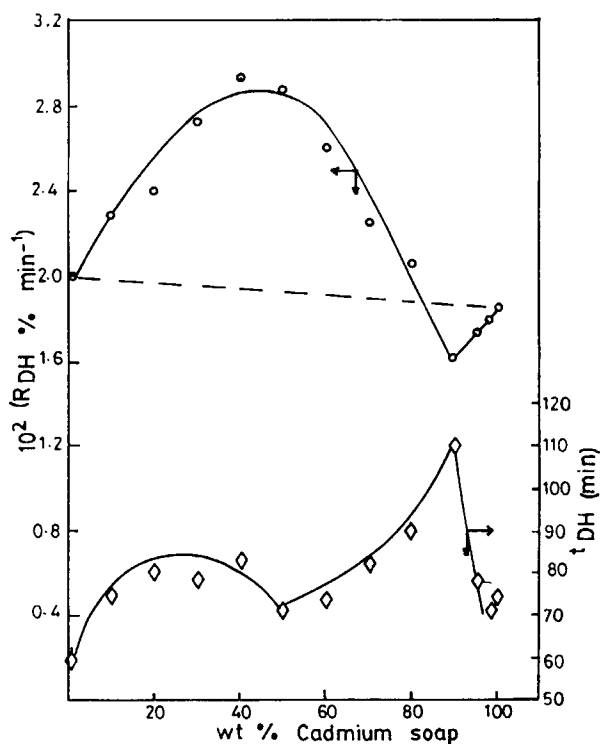


Figure 5 Dehydrochlorination of PVC in the presence of mixtures of barium and cadmium soaps of JSO at 190°C.

**Table II** Intrinsic Viscosities and Huggins Interaction Constant for PVC Degraded in the Presence of JSO Additives at 190°C

Additive	Time of Degradation (min)	$[\eta]$ (dL/g)	$K$	$[\eta]/[\eta]_0$
None	30	0.48	43.40	0.43
	60	0.39	46.02	0.35
	90	0.26	103.55	0.23
JSO (10 wt %)	30	0.71	21.48	0.63
	60	0.43	54.08	0.38
	90	0.32	87.91	0.29
EJSO (10 wt %) 5.6 mol % epoxidized	30	0.77	17.99	0.69
	60	0.55	27.84	0.49
	90	0.38	60.50	0.34
9.5 mol % epoxidized	30	0.83	16.33	0.74
	60	0.61	26.87	0.54
	90	0.45	49.38	0.40
Metal soaps from JSO (1 wt %) Barium soap	30	0.76	17.31	0.68
	60	0.62	24.71	0.55
	90	0.38	69.25	0.34
Cadmium soap	30	1.00	10.00	0.89
	60	0.71	19.84	0.63
	90	0.51	40.00	0.46

$[\eta]_0$  = intrinsic viscosity of undegraded PVC = 1.12.

The rates of dehydrochlorination of PVC at 190°C in the presence of mixtures of barium and cadmium soaps of JSO are shown in Figure 5. It can be seen that the effect of the soap mixtures on the degradation of PVC is not additive, showing antagonistic effects at mixture compositions up to 80 wt % cadmium and synergistic effects at a higher cadmium content of the mixture. The most deleterious (antagonistic) effect was observed at 40 wt % cadmium soap where the value of  $R_{DH}$  increased by about 50% from the ideal (additivity) value, while a remarkably improved stabilizing (synergistic) effect was found for the soap mixture containing 90 wt % cadmium with an  $R_{DH}$  value about 15% lower than the ideal value and a  $t_{DH}$  value about 51% higher than the ideal value.

The intrinsic viscosities of PVC and degraded samples were determined using the Huggins relationship:

$$\eta_{sp}/C = [\eta] + K[\eta]^2C \quad (1)$$

From the plots of  $\eta_{sp}/C$  against  $C$ , values of  $[\eta]$  and  $K$  were determined (Table II). Three types of reactions may take place during thermal degradation

of PVC, viz., dehydrochlorination, chain scission, and crosslinking, all of which should influence the viscosity of the polymer samples. Degraded PVC is semiflexible in nature, with the conjugated polyene sequence introduced in the polymer on dehydrochlorination constituting the rodlike part and with the undegraded portion being flexible. It has been reported that the intrinsic viscosity of PVC undergoing degradation decreases initially to a minimum and then increases with a further increase in the number of conjugated double bonds in the polymer.<sup>23</sup> In the present work, the extent of dehydrochlorination was kept low (5% conversion); therefore, the effect of double bonds on the intrinsic viscosity of the degraded PVC may be considered insignificant. The values of the relative intrinsic viscosity ( $[\eta]/[\eta]_0$ ) are generally lower than 1, indicating that in the presence of JSO additives, and for the extent of dehydrochlorination studied, chain scission rather than crosslinking may be the predominant reaction accompanying dehydrochlorination. It can be seen from the results that the extent of chain scission, like the  $R_{DH}$  values, is the least for degradation in the presence of metal soaps from JSO.

The results from this study suggest a potential application of metal soaps from JSO as thermal stabilizers for PVC. Corroborating evidence for the stabilizing effect of JSO on the degradation of PVC is being sought from the UV spectra of degraded PVC samples and will be discussed in future communications.

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