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THERMAL STABILISATION OF PVC WITH *JATROPHA* SEED, *KHAYA* SEED AND RUBBER SEED OILS. EFFECT OF BARIUM AND CADMIUM SOAPS OF THE SEED OILS ON THE THERMAL DEGRADATION OF PVC

F E Okieimen

University of Benin, Department of Chemistry, Benin City, Nigeria

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Polyvinyl chloride was mixed with barium and cadmium soaps of *Jatropha* seed, *Khaya* seed and rubber seed oils and mixtures of the metal soaps and degraded at 190˚C under oxidative and nonoxidative conditions. The effectiveness of the additives in stabilizing PVC against thermal degradation was evaluated by comparing (a) the kinetic data measured at 1% conversion for the degradation of PVC in the presence of the additives with the corresponding values obtained in the absence of the additives (b) the intrinsic viscosity and level of unsaturation in the polymer samples degraded for the undergraded polymer and (c) the thermogravimetric data obtained for the degradation of PVC in the presence of the additives at a constant heating rate of 10˚C min^{-1} up to 500˚C. It was found that the additives retarded the rate of dehydrochlorination of PVC (by up to about 50% and 1% conversion) and reduced the extent of decomposition of the polymer by as much as 60%. The mixtures of the metal soaps containing more than 70%(wt) cadmium soap showed marked synergistic stabilising effect on the degradation of PVC.

Key words**:** Thermal stabilisation, PVC synergistic effect, Metal soaps, Seed oils.

Introduction

Several workers (Bacaloglu and Fisch 1993, 1995; Geddes 1967; Iida and Goto 1980; Simen 1990; Simon and Valko 1990; Simon *et al* 1990; Varma and Sharma 1978; Verma *et al* 1987; Wypych 1986) have reported on the thermal degradation and stabilisation of PVC. At elevated temperatures well below its decomposition temperature, PVC loses HCl and becomes discoloured. Because these changes are accompanied by a deterioration in some of the useful properties of the polymer. It has become the practice to process PVC in the presence of heat stabilisers. Heat stabilising additives for PVC have been suggested to prevent or retard degradation reaction in a number of ways. Their proposed mechanism of action (Klemchuk 1968) include: (a) HCl scavenging; which is considered to preclude the autocatalytic effect of HCl on the degradation process, (b) modification of chain reactions leading to the inhibition of the elimination of HCl, (c) interrupting the formation of conjugated polyene sequence thus preventing the discolouration of the polymer, and (d) replacement of labile chlorine atoms within PVC structure with stabiliser moieties which are more stable to heat treatment. Heat stabilisers that have found commercial application in the processing of PVC include metal salts (soaps) of inorganic and organic acids, organometallic compounds and inhibitors of radical chain reactions. More recently interest has been shown in the use of poly epoxides (Hopff 1968) including epoxidised vegetable oils (May 1968; Okieimen 1999, 2000, 2001) and metal dicarboxylates (Ikhuoria *et al* 2001) as stabiliser for PVC. This report is part of on-going studies aimed at the development of industrially useful value-added products from local renewable resources and examines the stabilising effect of barium and cadmium soaps of *Jatropha multifida* seed, *Khaya senegalensis* seed and rubber seed oils on the thermal degradation of PVC. The physico-chemical characteristics and fatty acid composition of the seed oils (Aigbodion 1995; Eromosele 1998; Eromosele and Okieimen 1999; Okieimen and Okieimen 2001) have been presented in Table 1.

Experimental

Materials. PVC (BDH Ltd) ($\overline{Mn}$ 1.0 x 10^5, particle size of 100% passed B.S 60 mesh and 74% passed B.S 200) was purified by dissolution in THF/acetone and precipitation with constant stirring in a large excess of methanol. The precipitated polymer was filtered off after 24 h, washed with methanol and air-dried. *Jatropha* seed oil, JSO, was soxhlet - extracted with *n*-hexane from seeds collected in Benin City. *Khaya* seed oil, KSO was extracted with *n*-hexane from seeds collected from Michika, Adamawa; and rubber seed oil, RSO, was obtained from the Rubber Research Institute of Nigeria, Benin City.

Preparation of metal soaps from the seed oils. Metal soaps from the seed oils were prepared by metathesis in alcohol solution (Odilora 1989). Sodium soaps from the oils were first prepared by dissolving the oil sample (9.25g) in 50ml of hot ethanol followed by treatment with 20 ml of 20% (w/v)

Table 1

Physico-chemical characteristics and fatty acid composition of *Jatropha* seed, *Khaya* seed and Rubber seed oils

Parameter	Values		
	JSO	KSO	RSO
Physico-chemical characteristics			
Acid value (mg KOH/g)	5.61	24.00	23.00
Iodine value (gI2/100g)	157.37	68.00	155.56
Free fatty acid (%wt oleic acid)	2.70	7.64	11.26
Peroxide value (meq/kg)	5.11	26.00	0.40
Saponification value (mg KOH/g)	190.12	186.00	201.46
Specific gravity (at 30˚C)	0.92	0.96	0.93
Fatty acid composition (%wt)			
Caprylic acid	4.46	3.86	-
Myristic acid	2.61	1.64	2.20
Palmitic acid	20.57	19.05	7.60
Stearic acid	15.64	10.42	10.70
Arachiolic acid	5.68	2.04	-
Behenic acid	1.61	3.26	-
Pamitoleic acid	3.59	-	-
Oleic acid	32.87	54.34	20.61
Linoleic acid	5.25	-	36.62
Linolenic acid	-	-	22.50

sodium hydroxide solution. To its mixture, 100 ml of 30% (w/v) solution of the metal salts were added slowly with continuous stirring. The precipitated metal soap was washed with hot water and air-dried. Soaps were prepared using, $BaCl_2.2H_2O$ and $Cd(NO_3)_2.4H_2O$.

Degradation. Thermal degradation was carried out using PVC powder, mixed with 3%(wt) of the metal soaps of the oils. In a typical experiment, the polymer sample was mixed thoroughly with 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 60 ml/min. The degradation tube was immersed in a thermostat oil bath maintained at 190˚C and controlled to better than ± 1˚C. The HCl evolved was passed into a known volume of standard sodium hydroxide solution. The amount of HCl evolved was established by titration after various intervals of time. The extent of dehydrochlorination (%) was calculated from the ratio of HCl evolved to the amount available in the polymer.

Thermoxidative degradation was carried out in air as described for non-oxidative degradation except that dehydrochlorination rates were not monitored. Degradation was allowed to proceed for 30 min at the end of which the degradation tube was cooled down and the degraded polymer was recovered and stored in the dark.

Viscosity measurement. The degraded PVC samples were purified by dissolution in cyclohexane and precipitation in a large excess of methanol. The precipitated polymer was filtered off, washed several times with methanol and dried in vacuum at room temperature. The viscosities of the solutions of degraded polymer samples in cyclohexane were measured at 30˚C. Intrinsic viscosities were determined from the measured viscosities using the relationship (Huggins 1942) is as under

$$\frac{\eta_{sp}}{C} = [\eta] + k_H [\eta]^{-2} C \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Here, C is the concentration of the polymer solution in g/dl; η_{sp}/C is reduced viscosity calculated from the relationship $\eta_{sp}/C = (\eta_{rel} - 1)$ and $\eta_{rel} = \eta_{soln}/\eta_{solv} \cong t/t_o$; where 't' is the time of flow of polymer solution and 't_o' is the time of flow of solvent at the temperature of measurement, $[\eta]$ is the intrinsic viscosity, measured at $\eta_{sp}/C \lim C \rightarrow O$ and k_H is the Huggin's constant.

Determination of level of unsaturation in degraded PVC samples. The levels of unsaturation in the degraded PVC samples were determined by measuring the iodine values using the Wij's method (BSI 1976).

Thermogravimetric study of PVC degradation. A Perkin-Elmer TGA-7 Thermal Gravimetric Analyser (TGA) programmed at a heating rate of 10˚C min^{-1} up to 500˚C was used for studying, (a) barium and cadmium soaps of KSO, (b) unstabilised PVC, (c) PVC stabilised with barium and cadmium soaps of KSO and (d) PVC stabilised with admixtures of barium and cadmium soaps of KSO. About 150mg of PVC sample was mixed thoroughly with a known amount of the additive in a motar and an aliquot was carefully transferred into the platinum pan and placed in the TGA. The change in sample weight was recorded automatically as a function of temperature.

Results and Discussion

Nonoxidative degradation. The rates of dehydrochlorination of PVC at 190˚C in the presence of barium soaps of the seed oils are shown in Fig 1. Similarly, plots were obtained for the degradation of PVC in the presence of cadmium soaps of the oils. The rates of dehydrochlorination at 1% conversion, R_{DH}, were determined and the time required for degradation to attain 1% conversion t_{DH} was noted. The effect of the metal soaps of the seed oils on the thermal degradation of PVC was evaluated by comparing the values of t_{DH} and R_{DH} with the corresponding values, t^o_{DH} and R^o_{DH}, obtained in the absence of the metal soaps of the seed oils (i.e. t_{DH}/t^o_{DH} and R_{DH}/R^o_{DH}) and have been shown in Table 2. For an additive to be considered an effective stabiliser for PVC, the value of $t_{DH}/$

Table 2

Non-oxidative thermal degradation of PVC at 190°C in the presence of barium and cadmium soaps of seed oils

	t_{DH}/t^o_{DH}			R_{DH}/R^o_{DH}			$[\eta]/[\eta]_o$			$(IV)/(IV)_o$		
Additive	JSO	KSO	RSO	JSO	KSO	RSO	JSO	KSO	RSO	JSO	KSO	RSO
Barium soap	1.90	1.13	1.69	0.70	0.73	0.83	0.60	-	0.73	-	-	12.00
Cadmium soap	2.39	2.00	1.80	0.65	0.58	0.67	0.87	-	0.63	-	-	11.00

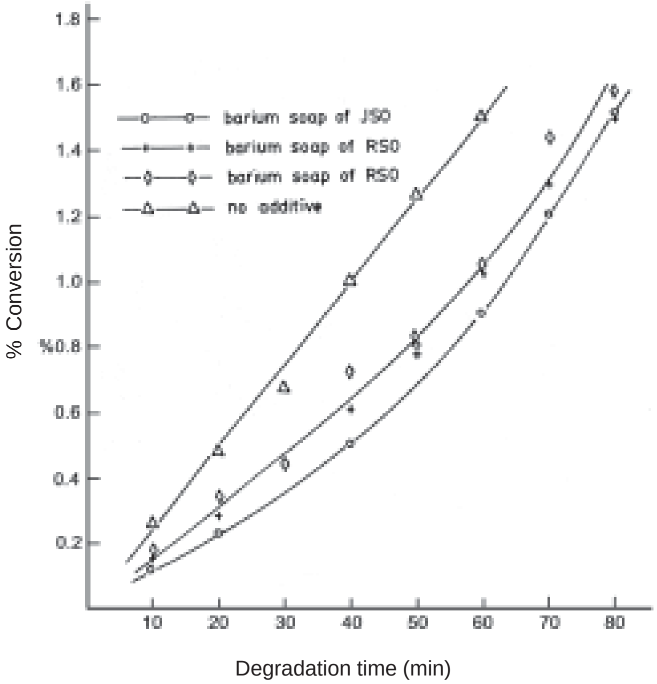

Fig 1. Non-oxidation dehydrochlorination of PVC in the presence of barium soaps of seed oils at 190°C.

t^o_{DH} should be greater than 1, and the values of R_{DH}/R^o_{DH} should be less than 1, the greater the divergence of the values from unit, the more effective the additive is considered in stabilising PVC against thermal dehydrochlorination. The result (Table 2) shows that the metal soaps of the seed oils are relatively effective in stabilising PVC against thermal degradation and that the cadmium soaps of the seed oils are more effective stabilisers than the barium soaps. The stabilising effect of the metal soaps is considered to be due to their facile reaction with HCl and substitution of labile chlorine atoms within PVC structure with additive moieties (Klemchuk 1968; Frye and Horst 1959). Cadmium soaps are generally considered more reactive than the corresponding barium compounds and consequently would be expected to be more effective stabi-lising PVC against thermal degradation. In a previous study (Okieimen 1999), it was reported that derivatives of rubber seed were more effective than the corresponding derivatives of unsaturated fatty acids (oleic and linoleic acids) in stabi-lising PVC against thermal degradation and explanations in terms of the contribution of the chemical identity (level of unsaturation) of the hydrocarbon moiety of the fatty acids to the overall stabilisation process were proffered. It has been suggested that the nature of the hydrocarbon portion of the fatty acid may influence PVC stability by altering the polymer matrix polarity (Starnes 1994). However, the result in Table 2 does not suggest any relationship between the levels of unsaturation of the seed oils and the stabilising effect of their metal soaps.

The intrinsic viscosity of PVC samples degraded at 190°C under nitrogen for 30 min in the presence of barium and cadmium soaps of the seed oils are presented in Table 2. Degraded PVC is semi-flexible in nature, with the conjugated polyene sequence in the polymer, following dehydrochlorination, constituting the rod-like part and the undegraded portion being flexible. It has been suggested (Okieimen 2000) that at low extents of dehydrochlorination (≤ 5% conversion) changes in the values of intrinsic viscosity correlate closely with the extent of degradation: the lower the value of intrinisic viscosity, the greater the extent of degradation. Therefore, the value of relative intrinsic viscosity, $[\eta]/[\eta]_o$, where $[\eta]_o$ is intrinsic viscosity of undegraded PVC can be used to evaluate the effect of additives on the degradation. The reactions that may accompany thermal dehydrochlorination of PVC include chain scission, which will be associated with reduction in the value of intrinsic viscosity and crosslinking which should lead to higher values on intrinsic viscosity. The intrinsic data in Table 2 show that the barium and cadmium soaps of the seed oils exert stabilising effect on the degradation of PVC and that chain scission may be the predominant reaction accompanying dehydrochlorination of PVC under the conditions of this study.

The elimination of HCl during thermal degradation of PVC leads to the formation of olefinic double bonds in the polymer molecule. Therefore, it is provided that the extent of degradation is low and dehydrochlorination is not accompanied by secondary reactions involving the double bonds, measurement of the level of unsaturation in the degraded polymer sample should provide satisfactory estimate of the relative

Table 3
Thermoxidative degradation of PVC at 190°C in the presence of metal soaps of seed oils

	$[\eta]/[\eta]_0$			$(IV)/(IV)_0$		
Additive	JSO	KSO	RSO	JSO	KSO	RSO
O	0.43	0.43	0.43	-	-	17.37
Barium soap	0.52	0.80	0.61	-	-	11.84
Cadmium soap	0.67	0.89	0.89	-	-	8.85

Degradation time = 30 min

stabilising ability of additives. The ratio of the iodine value of degraded PVC sample to the value of undegraded sample, $(IV)/(IV)_o$, can be used to assess the relative effect of the additives on the thermal degradation of PVC: the smaller the $(IV)/(IV)_o$ value, the greater the relative stabilising ability of the additive. The levels of unsaturation of PVC samples degraded at 180°C for 30 min in the presence of barium and cadmium soaps of the seed oils have been shown in Table 2. The results show a decrease of more than 40% in iodine value relative to the value obtained for unstabilised PVC. These results clearly show that the addition of the additives to PVC reduce the levels of unsaturation in the degraded polymer and indicate a stabilising effect of the additives on the thermal degradation of PVC.

Thermoxidative degradation. The intrinsic viscosity and levels of unsaturation of PVC samples degraded in air at 190°C for 30 min in the presence of barium and cadmium soaps of the seed oils are shown in Table 3. The results show that the values of intrinsic viscosity of the degraded PVC samples are lower than the value for the undegraded sample. The values of intrinsic viscosity of PVC samples degraded in the presence of barium and cadmium soaps of the seed oils are much higher (by between 30 and 60%) than the value obtained for the sample degraded in the absence of the additives. These results indicate that the extent of degradation of PVC in the presence of the additives is smaller than in the absence of the additives. The levels of unsaturation of PVC samples degraded in and at 190°C for 30 min have been shown in Table 3. The values of $(IV)/(IV)_o$ obtained for the polymer samples degraded in the presence of barium and cadmium soaps of the seed oils are 50% higher than the value obtained for PVC sample degraded in the absence of the additives. These results indicate that barium and cadmium soaps of the seed oils are effective in stabilising PVC against thermoxidative degradation.

Degradation in the presence of binary mixtures of barium and cadmium soaps of the seed oils. The effect of binary mixtures of barium and cadmium soaps of the seed oils on the thermal degradation of PVC was examined at 190°C under-oxidative and oxidative conditions. The variations of the values of R_{DH} and t_{DH} with composition of the soap mixtures are shown in Table 4. The results show that the effect of the mixtures of the metal soaps is not additive. The initial increase in the values of R_{DH} with increase in the cadmium soap content of the mixture attained maximum values at between 40-60%(wt) and thereafter, decreased with further increase in the cadmium soap content of the mixture. Minimum R_{DH} values of 1.62×10^{-2} % min^{-1} and 1.33×10^{-2} % min^{-1} were obtained at 90%(wt) cadmium soap content of the soaps mixtures of JSO and RSO, respectively. Similarly, maximum t_{DH} values of 110 min and 101 min were obtained at 90 % (wt) cadmium soap content of soap mixture of JSO and RSO, respectively. These results show that barium and cadmium soaps

Table 4
Effect of mixture of barium and cadmium soaps of seed oil on the thermal degradation of PVC at 190°C

Composition of soap mixture (%Cd soap)	$10^2 R_{DH}(\%min^{-1})$		t_{DH} (min)		$[\eta]/[\eta]_o^*$		$(IV)/(IV)_o^*$	
	JSO	RSO	JSO	RSO	JSO	RSO	JSO	RSO
0	2.00	1.67	59.00	69.50	0.27	-	17.36	15.51
10	2.28	1.81	74.00	69.80	0.52	0.48	10.69	11.62
20	2.40	1.91	80.00	75.00	0.61	0.34	10.39	10.47
30	2.72	1.95	79.00	65.00	0.40	0.69	10.22	9.84
40	2.92	1.97	51.00	75.00	0.35	0.73	10.04	9.42
50	2.88	2.08	71.00	69.00	0.46	0.76	9.87	8.99
60	2.60	2.00	74.00	75.00	0.50	0.83	9.62	8.16
70	2.24	1.79	82.00	74.00	0.64	0.87	9.36	7.74
80	2.06	1.54	90.00	89.00	0.67	0.94	9.10	7.32
90	1.62	1.23	110.00	101.00	0.70	1.00	8.52	6.27
95	1.75	1.40	78.00	98.00	0.56	0.97	8.67	9.85
100	1.82	1.43	74.00	80.00	0.54	0.89	8.67	8.99

*Polymer samples degraded for 30 min in air.

Table 5

Thermogravimetric evaluation of relative stabilising effect of metal soaps of KSO on the thermal degradation of PVC

Additive	%Weight loss		Residue	t_{dmax}(°C)	Temperature at which degradation was attained (°C)	
	Stage I	Stage II			1%	5%
None	64.75	18.82	16.42	302.50	256.80	281.80
Barium soap of KSO	59.18	9.30	31.62	322.30	260.00	295.40
Cadmium soap of KSO	62.06	11.03	26.90	328.50	262.10	297.50
Mixture of Ba and Cd Soaps of KSO						
% Cd soap content						
10	61.23	10.02	28.75	324.40	268.30	304.70
50	60.59	10.59	28.84	328.40	274.60	301.60
90	60.49	9.99	29.90	329.50	276.60	303.70

of the seed oils exhibit synergistic stabilising effect on the thermal degradation of PVC. The combined effect of barium and cadmium soaps of the seed oils in stabilising PVC against thermal degradation can be described as monosynergism, i.e. synergism involving compounds of unequal activity that operate by the same mechanism. The reaction sequence include (David 1975; Onozuka & Asahina 1969) (a) facile reaction of the more reactive component (cadmium soap) with labile chlorine atom in PVC, (b) conversion of the cadmium chloride to the soap be reacted with barium soap; and (c) scavenging of the HCl formed during the early stages of dehydrochlorination. The reaction that is considered most critical for the synergistic stabilising effect of the soap mixture is the reaction between cadmium chloride and barium soap (David 1975; Onozuka & Asahina 1969). Although, the stiochiometry of the reactions, particularly the ester exchange reaction between cadmium chloride and barium soap taking place in the polymer matrix is not fully understood, the result (Table 4) indicates that barium and cadmium soap mixtures of the seed oils formulated to contain 90%(wt) cadmium soap would be effective in stabilising PVC against thermal degradation.

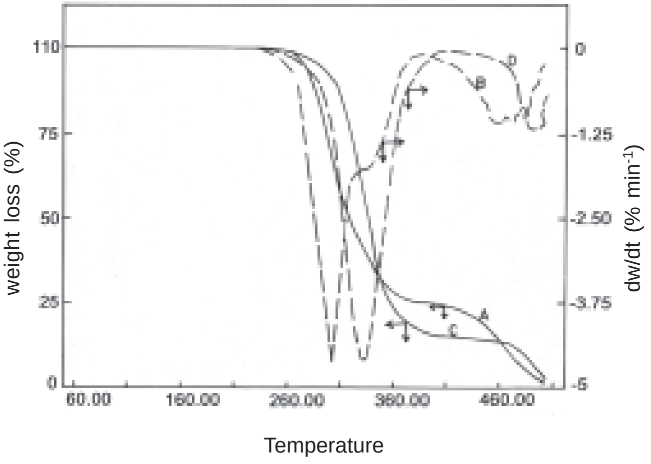

Fig 2. Thermograms of unstabilised PVC A-TG, B-DTG and PVC stabilised with cadmium soap of KSO C-TG, D-DTG.

The variations of the values of intrinsic viscosity and iodine value of PVC samples degraded in air at 190°C for 30 min have been shown in Table 4. The results show that mixture of barium and cadmium soaps of the seed oils exhibit antagonistic stabilising effect on the degradation of PVC at soap mixture composition up to about 60%(wt) cadmium soap and synergistic effect at higher cadmium soap content of the mixture.

Thermogravimetric studies on PVC degradation. The thermograms for unstabilised PVC stabilized with cadmium soap of KSO are shown in Fig 2. Similar thermograms were obtained for PVC stabilized with barium soap of KSO and PVC stabilized with mixtures of the soap. The values of weight loss of the polymer sample during degradation and the temperature at which maximum rates of degradation occurred, t_{dmax} were recorded automatically by the TG analyser and are shown in Table 5. The relative stability of PVC was also evaluated from the temperatures at which various extents of degradation (1 and 5%) occurred and shown in Table 5. The results show that the metal soaps of KSO reduce the extent of thermal degradation of PVC and that mixtures of barium and cadmium soaps of KSO exhibited synergistic stabilising effect on the degradation process.

Conclusion

This study examined the effect of barium and cadmium soaps of *Jatropha* seed, *Khaya* seed and rubber seed oils on the degradation of PVC using rate, viscosity and iodine value measurements as well as thermogravimetric studies. The results show that the metal soaps of the seed oils retard dehydrochlorination rates and reduce the extent of degradation of PVC. Synergistic stabilising effect on thermal degradation was barium and cadmium soaps of the seed oils. These results demonstrate potential application of the derivatives of the seed oils as stabilizer in PVC formulations.

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