Thermal Stabilization of PVC with Khaya Seed Oil: Thermogravimetric Studies

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ABSTRACT: Thermal degradation of PVC stabilized with barium and cadmium soaps of *Khaya senegalensis* seed oil was studied by thermogravimetry up to 500°C using a constant heating rate of 10°C min^{-1}. At temperatures below 300°C, the extents of dehydrochlorination of both the unstabilized and stabilized PVC samples were low (less than 6% conversion). It was found from the values of weight loss that HCl was the only volatile product of degradation of PVC between 170 and 200°C. The rates of dehydrochlorination at about 200°C was of the order of 10^{-2}% min^{-1}, about the same order of magnitude as the values obtained from kinetic studies. The temperatures at which maximum rates of degradation were attained, $t_{d\max}$, and the temperatures at which various extents of degradation were attained were used to assess the effectiveness of the metal soaps of Khaya seed oil in stabilizing PVC against thermal degradation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1432–1438, 2000

Key words: thermogravimetry; stabilization; PVC; Khaya seed oil

INTRODUCTION

Several workers[1–10] have reported on the thermal degradation and stabilization of PVC. At elevated temperatures well below its decomposition temperature, PVC loses HCl and becomes discolored. Because the changes accompanying degradation are associated with deterioration in the properties of the polymer, it has become the practice to process PVC in the presence of heat stabilizers. 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 stabilizing effects of derivatives (epoxides and metal soaps) of rubber seed oil[11–13] and Jatropha seed oil,[14–16] using data from rate measurements at 1% conversion and changes in viscosity data. Because kinetic and viscometric data reports do not provide information about the nature and chemical structure of intermediate products of degradation, we, in the present report, examined the effect of barium and cadmium soaps of *Khaya senegalensis* (KSO) seed oil and their admixtures on the thermal degradation of PVC using thermogravimetric analysis (TGA). The physicochemical characteristics and fatty acid composition of KSO seed oil[17,18] are shown in Table I.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) (BDH Ltd; M_n 1.0 $\times$ 10^5; particle size of 100% passed 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.

Table I Physicochemical Characteristics and Fatty Acid Composition of KSO[17,18]

Characteristics	Values
Specific gravity (at 30°C)	0.962
Free fatty acid (% as oleic acid)	7.62
Acid value (mg KOH/g)	24.0
Peroxide value (meq/kg)	26.0
Iodine value (g I$_2$/100 g)	68.0
Saponification value (mg KOH/g)	186.0
Fatty acid composition (%)	
Arachidic acid	2.04
Behenic acid	3.26
Caprylic acid	3.82
Lignoceric acid	0.90
Myristic acid	1.64
Palmitic acid	19.05
Stearic acid	10.42
Oleic acid	54.34

The precipitate polymer was filtered off after 24 h, washed with methanol, and air-dried. KSO seed oil was Soxhlet-extracted with *n*-hexane from the seed (meal) obtained from Michika district, Adamawa State, Nigeria.

Preparation of Metal Soaps of KSO

The metal soaps of KSO were prepared by metathesis in an alcohol solution.[19–21] The sodium salt of KSO was first prepared by dissolving the oil (9.2 g) in hot ethanol. A stoichiometric amount of a sodium ethoxide solution was then added to the mixture and an equivalent concentration of the metal salt solution was continuously stirred into the mixture. The precipitated metal soap was washed with hot water and recrystallized from hot benzene.[22,23] The salts used were Cd(NO$_3$) · 4H$_2$O and BaCl$_2$ · 2H$_2$O.

### Determination of Stability of PVC Samples Using TGA

A Perkin-Elmer TGA-7 thermal gravimetric analyzer programmed at a heating rate of 10°C min^{-1} up to a temperature of 500°C was used for the TGA studies.

RESULTS AND DISCUSSION

Thermogravimetric (TG) studies were conducted on (i) barium and cadmium soaps of KSO, (ii) unstabilized PVC, (iii) PVC stabilized with bar-

ium and cadmium soaps of KSO, and (iv) PVC stabilized with mixtures of barium and cadmium soaps of KSO. The thermal behavior of barium and cadmium soaps of KSO at a constant heating rate of 10°C min^{-1} up to 500°C was investigated. Thermograms, TG and DTG, of barium soap of KSO are shown in Figure 1. Similar thermograms were obtained for the cadmium soap of KSO. It was found that at temperature up to 200°C the metal soaps of KSO were relatively stable, with a weight loss of about 6 and 1.5%, respectively, for barium soap and cadmium soap of KSO. It would appear from the DTG curves that the metal soaps of KSO undergo a three-stage process when subjected to heat treatment: elimination of water molecules associated with the soap with maximum dw/dt values at 100–110°C, a transition process with a maximum rate at 260°C, and decomposition of the metal soaps with the maximum rate occurring at about 460 and 500°C, respectively, for cadmium soap and barium soap of KSO. For an additive to be effective in stabilizing a polymer against thermal degradation, it is required that the additive should be stable within the processing temperature range of the polymer. The weight loss observed for the metal soaps at moderate temperatures (about 200°C) suggests that within the range of temperatures frequently used in the processing of PVC (200–250°C) that barium and cadmium soaps of KSO would be stable and therefore will be effective in stabilizing PVC against thermal degradation.

The TG and DTG curves for the unstabilized PVC sample and the PVC stabilized with cadmium soap of KSO are shown in Figures 2 and 3, respectively. Similar thermograms were obtained for PVC stabilized with barium soap of KSO and for PVC stabilized with mixtures of the soap. The values of weight loss for stages one and two of the degradation process were recorded automatically by the TG analyzer and are shown in Table II. In stage one of the degradation process, dehydrochlorination is considered to be the main reaction and HCl is assumed to be the major volatile product of degradation, while in stage two, elimination of low molecular weight hydrocarbon molecules such as benzene, toluene, etc., contribute to the measured weight loss of the polymer. However, oxidation scission of the polyene sequence followed by the elimination of low molecular hydrocarbon molecules occurs simultaneously with the volatilization of HCl during stage one[24] and is associated with weight loss greater than the theoretical value, based on dehydrochlorination of
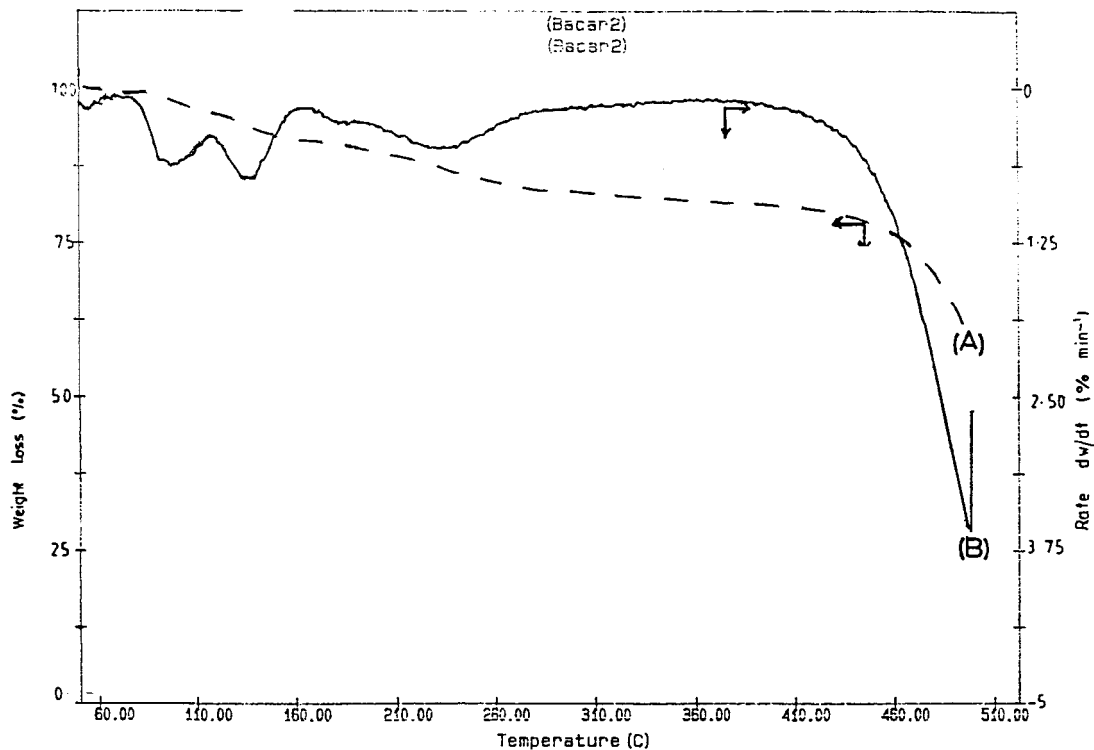
Figure 1   Thermogram of barium soap of KSO: (- - -) curve (A), TG curve; (—) curve (B), DTG curve.
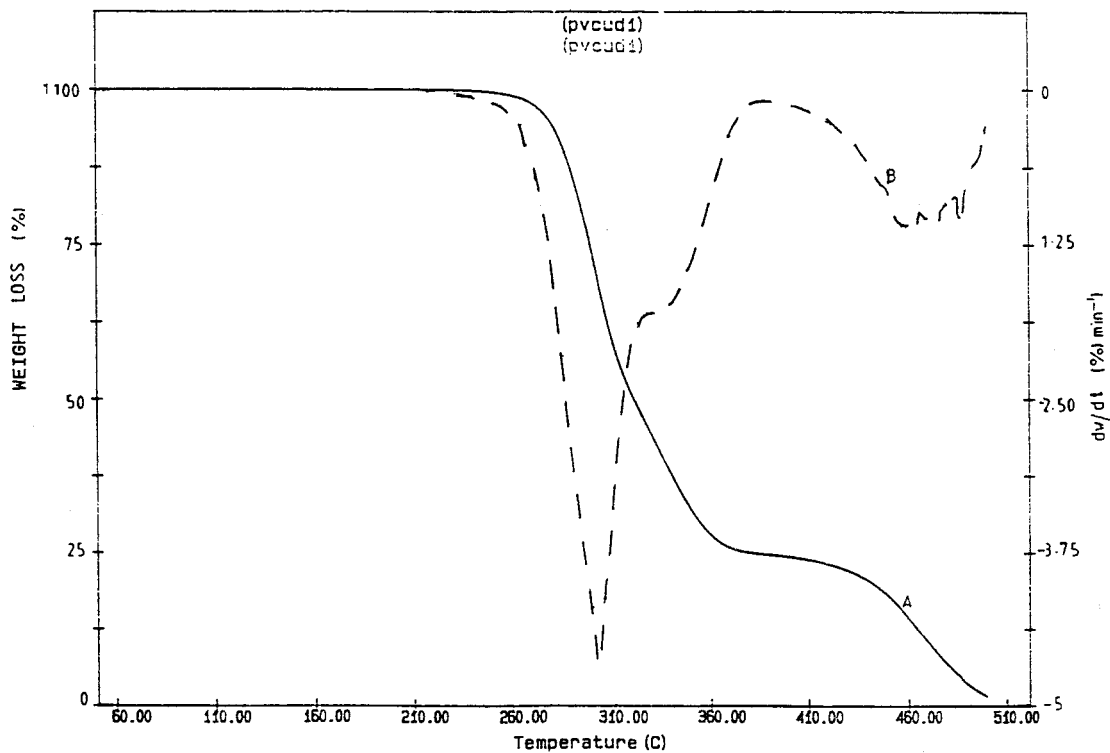
Figure 2   Thermogram of unstabilized PVC: (—) curve (A), TG curve; (- - -) curve (B), DTG curve.
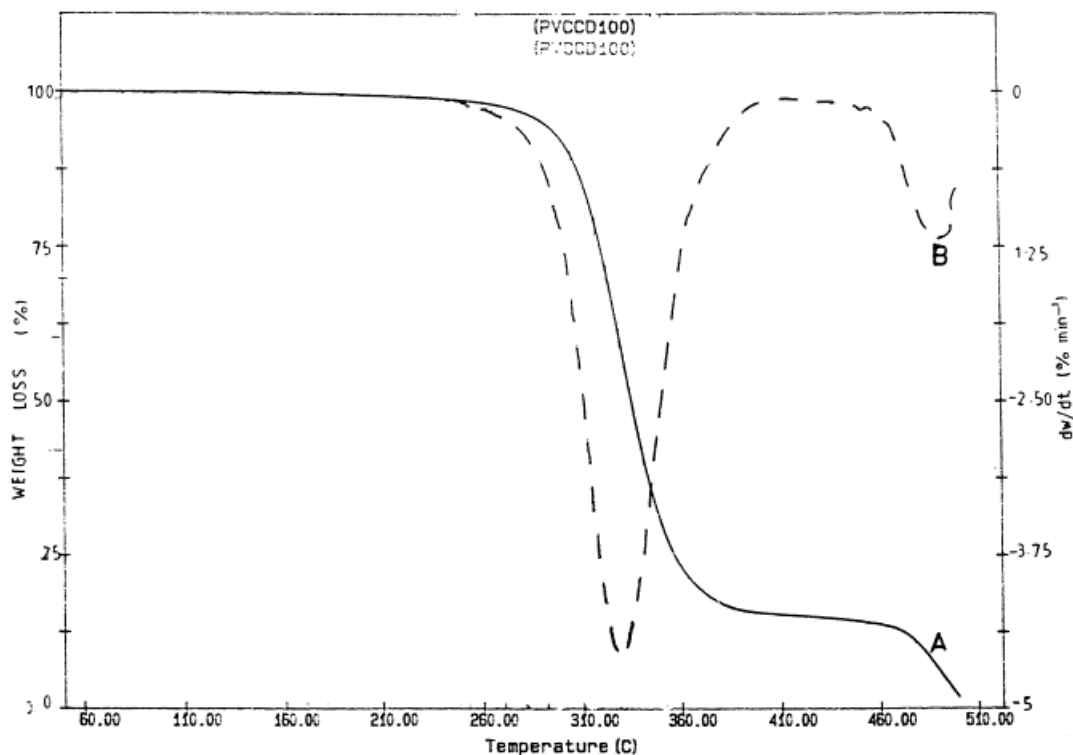
Figure 3 Thermogram of PVC stabilized with cadmium soap of KSO: (—) curve (A), TG curve; (- - -) curve (B), DTG curve.

the polymer. The behavior of PVC during the stage one process is of a more direct interest in stabilization studies. It can be seen (Table I) that the percentage weight loss of PVC stabilized with metal soaps of KSO in the largely dehydrochlorination phase of the degradation process is generally lower than is the value for the unstabilized polymer. The results show that the PVC sample stabilized with the mixture of the soap containing 90 wt % cadmium soap showed the lowest weight loss. Similar results were obtained from kinetic and viscosity data on the degradation of PVC in the presence of binary mixtures of barium and cadmium soaps of rubber seed oil[13] and were explained in terms of synergism of barium and cadmium compounds in stabilizing PVC against thermal degradation.

The temperature at which maximum rates of degradation occurred, $t_{d\max}$, was recorded automatically by the TG analyzer and is shown in

Table II   TG Data (% Weight Loss) of PVC During Thermal Degradation

Additive	% Weight Loss		% Residue
	Stage I	Stage II	
None	64.75	18.82	16.42
Barium soap of KSO	59.18	9.30	31.62
Cadmium soap of KSO	62.06	11.03	26.90
Mixture of barium & cadmium soap of KSO: % cadmium soap content			
10	61.23	10.02	28.75
50	60.59	10.59	28.84
90	60.49	9.99	29.90

Table III   Evaluation of Relative Thermal Stability of PVC Stabilized with Metal Soaps of KSO at Temperature at Which Various Extents of Degradation Were Attained

Additive	$t_{d\max}$ (°C)	Temperature at Which Degradation Was Attained (°C)				
		1%	5%	10%	30%	50%
None	302.5	256.8	281.8	291.2	307.9	336.0
Barium soap of KSO	322.3	260.0	295.4	310.0	331.2	345.6
Cadmium soap of KSO	328.5	262.1	297.5	312.1	332.5	349.2
Barium/cadmium - soap mixtures of KSO						
10 wt % cadmium soap	324.4	268.3	304.7	332.5	345.8	357.0
50 wt % cadmium soap	328.4	274.6	301.6	349.2	346.6	351.4
90 wt % cadmium soap	329.5	276.6	303.7	314.1	338.1	352.5

Table III. The relative stability of PVC containing the metal soaps of KSO was also evaluated from the temperatures at which various extents of degradation (1–50%) occurred.[25] The values of $t_{d\max}$ for unstabilized PVC was found to be 302°C, while the values for PVC stabilized with barium and cadmium soaps of KSO were 322 and 328°C, respectively. The PVC sample stabilized with the

Table IV   TG Kinetic Data on PVC Degradation

Additive	Temperature (°C)	Rate of Degradation $10^2 R_{DH}$ (% min^{-1})	Activation Energy (kJ mol^{-1})
None	210	4.51	
	230	9.02	89.2
	240	18.04	
	250	27.06	
Barium soap of KSO	210	4.50	
	230	9.00	80.2
	240	13.53	
	250	18.04	
Cadmium soap of KSO	210	9.20	
	230	13.50	57.3
	240	18.00	
	250	27.10	
Mixtures of barium & cadmium soap of KSO: % cadmium soap contents			
10	210	4.50	
	230	4.50	84.3
	240	9.00	
	250	13.33	
50	250	9.00	157.2
	260	18.00	
	270	36.10	
90	230	4.51	112.2
	240	9.02	
	250	13.53	
	260	18.04	

soap mixture containing 90 wt % cadmium soap showed the highest $t_{d\max}$ value of 329°C. It can be seen from the results in Table II that the temperatures at which the various extents of degradation occurred were lower for the unstabilized PVC than for the corresponding values for PVC stabilized with metal soaps of KSO.

The rates of degradation of PVC at various temperatures were obtained from the DTG curves for the unstabilized and stabilized polymer samples (Table IV). The activation energy for the degradation process was evaluated from the DTG data using the method described by Friedman.[26] The overall activation energy for dehydrochlorination of PVC under a nitrogen atmosphere was reported[27,28] to lie within the range 105–146 kJ mol^{-1} for dry PVC, with a mean value of about 116 kJ mol^{-1}. However, under an oxygen atmosphere, markedly lower values (50–83 kJ mol^{-1}) were reported[29,30] for PVC. Values of activation energy for unstabilized and lead dodecanoate-stabilized PVC of 37 and 40 kJ mol^{-1} were reported by Odilora.[22] The factors that influence the value of activation energy include molecular weight and molecular weight distribution of the polymer, the polymerization process, and the nature and amount of impurities contained in the polymer. The values from this study more or less fall within this broad range except for PVC stabilized with cadmium soap of KSO which gave a value of 57 kJ mol^{-1}. It might be expected that the addition of a heat stabilizer to PVC should result in higher values of activation energy for dehydrochlorination and that the more effective the heat stabilizer the higher the activation energy values. Although Fernandez et al.[31] reported that the values of activation energy determined by the Friedman method compared favorably with the values obtained from using the methods described by Kissinger,[32] Flynn and Wall,[33] and Reich,[34] it is to be noted that degradation was examined by thermogravimetry, a nonisothermal process, and that the Arrhenius-type method may not provide reliable values for activation energy from the measured values of the rate of degradation.

CONCLUSIONS

The results from the thermal behavior of barium and cadmium soaps of KSO and the effect of the metal soaps on the thermal behavior of PVC show that the additives have a potential application as a costabilizer for PVC.

REFERENCES

1. Ivan, B.; Kelen, T.; Tudos, F. In Degradation and Stabilisation of Polymers; Jellinek, H.H.G., Ed.; Elsevier: New York, 1989; Vol. 2.
2. Starnes, W. H., Jr. Polym Prepr Am Chem Soc 1994, 35, 425.
3. Danforth, J. D.; Takeuchi, T. J Polym Chem Ed 1973, 11, 2083.
4. Asahina, M.; Onozuka, M. J Polym Sci A 1964, 2, 3505.
5. Simon, P. Polym Degrad Stabil 1990, 29, 155.
6. Braun, D. In Development in Polymer Degradation, Grassie, N., Ed.; Applied Science: London, 1981; Vol. 3.
7. Hoang, V. T.; Michel, A.; Guyot, A. Polym Degrad Stab 1982, 4, 213.
8. Hopff, H. In Stabilisation of Polymer and Stabiliser Processes; Advances in Chemistry Series 85; Gould, R. F., Ed.; American Chemical Society, Washington, DC, 1986.
9. Hjertberg, T.; Sorvik, E. M. In Degradation and Stabilisation of PVC; Owen, E. D., Ed.; Elsevier: London, 1984.
10. Guyot, A.; Michel, A. Dev Polym Stab 1980, 2, 89.
11. Okieimen, F. E.; Ebhoaye, J. E. Eur Polym J 1992, 28, 1423.
12. Okieimen, F. E.; Ebhoaye, J. E. Angew Makromol Chem 1993, 206, 1.
13. Okieimen, F. E.; Ebhoaye, J. E. J Appl Polym Sci 1993, 48, 1953.
14. Okieimen, F. E.; Sogbaike, C. E. J Appl Polym Sci 1995, 57, 513.
15. Okieimen, F. E.; Sogbaike, C. E. Eur Polym J 1996, 32, 1457.
16. Okieimen, F. E. Niger J Appl Sci 1996, 15, 84.
17. Okieimen, F. E.; Eromonsele, O. C. Biores Technol 1999, 69(3), 279.
18. Ogbobe, O.; Akano, V. I.; Ozoh, N. G. Riv Ital Sostanze Grasse 1993, 80, 253.
19. Vold, R. D.; Hattiangdi, G. S. Ind Eng Chem 1949, 41, 2311.
20. Adeosun, S. O.; Sime, S. J. Thermochim Acta 1976, 17, 351.
21. Burrows, H. D.; Ellis, H. A.; Akamni, M. S. In Proceedings of the Second European Symposium on Thermal Analysis; Dallimore, D., Ed.; Heyden: London, 1981; pp 302–305.

22. Odilora, C. A. Acta Polym 1989, 40, 541.

23. Odilora, C. A. Acta Polym 1990, 41, 71.

24. Stromberg, R.; Straus, S.; Achhammer, B. G. J Polym Sci 1959, 35, 355.

25. Jefferys, K. D. Brit Plast 1963, 36, 188.

26. Friedman, H. L. J Polym Sci C 1965, 6, 183.

27. Varma, I. K.; Grover, S. J Appl Polym Sci 1970, 14, 2965.

28. Talamini, G.; Pezzin, G. Makromol Chem 1960, 39, 26.

29. Arlman, E. J. J Polym Sci 1954, 12, 547.

30. Bacologlu, R.; Fisch, M. Polym Degrad Stab 1994, 45, 301.

31. Fernandez, M. J.; Fernandez, M. D.; Casinos, I.; Guzman, G. M. J Polym Sci Polym Chem 1989, 27, 3173.

32. Kissinger, H. E. Anal Chme 1957, 29, 1702.

33. Flynn, J. H.; Wall, L. A. J Polym Sci B 1966, 4, 323.

34. Reich, L. J Polym Sci B 1964, 2, 621.