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Metal soaps of *Hura crepitans* seed oil: Potential stabilizer for unplasticised polyvinyl chloride against thermal degradation

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ABSTRACT

The effect of metal soaps of *Hura crepitans* seed oil prepared using Cd, Ba, Zn and Ca salts on thermal stability of unplasticised polyvinyl chloride (UPVC) films obtained by solvent casting is reported. The results show that the derivatives of the seed oil exert stabilizing effect on the UPVC against thermal degradation. The effectiveness of the metal soaps was found to be in the order: Cd > Ba > Zn > Ca. The mechanism of stabilization may probably be due to the replacement of labile chlorine atoms within the polymer structure with carboxylate groups which are more stable to heat treatment.

1. Introduction.

Polyvinyl chloride (PVC) is thermally unstable and degrades due to heat and aging. The phenomenal result of degradation includes colour change, cracking, embrittlement and general loss of desirable properties. Thermal degradation of PVC is generally considered to be initiated at unstable, particularly tertiary and allylic chlorides sites within the structure of the polymer and has been reported [1 – 5] that these structural irregularities are responsible and can account for the low thermal stability of PVC.

The solution to the inherent problem of low thermal stability of the polymer is the use of stabilizers in processing of the material. Additives that have proved useful as thermal stabilizers include metal salts of organic acids, organometallic compounds and inhibitors of radical chain reactions. Recently, the use of rubber seed oil, epoxidised rubber seed oil and metal soaps (cadmium,barium and lead) of these oils as stabilizers for PVC has been reported [6]. Aromatic hydrazides and their derivatives have been investigated as thermal stabilizers for rigid polyvinyl chloride (PVC) at 180 °C in air by measuring the rate of dehydrochlorination and the extent of discoloration of the degraded polymer [7]. Mohamed and Al-Magribi [8] have reported several N-(substituted phenyl)itaconimide derivatives to be effective thermal stabilizers for rigid PVC. The stabilizing efficiency of N-(RPh)II derivatives were attributed to the replacement of the labile chlorines on the PVC chains by relatively more thermally stable stabilizer moieties. The effectiveness of benzal thiobarbituric acid (BTBA) and some of its derivatives [9], phenylurea and phenylthiourea derivatives [10], mixed metal stearates [11], N-Arylphthalimides derivatives [12], barium and cadmium soaps of *Khaya senegalensis* seed oil [13],crotonal thiobarbituric acid (CTBA) and cinamal thiobarbituric acid (CiTBA) [14], barium, cadmium and lead soaps of the epoxidised *Jatropha* seed, *Khaya* seed and rubber seed oils [15], Zinc soaps of rubber seed oil (RSO) and epoxidised rubber seed oil (ERSO) [16] to mention but a few as thermal stabilizers for rigid PVC can be found in the literature.

Hura crepitans whose seed oil is the main focus of the present investigation belongs to the family Euphorbiaceae [17]. Preliminary reports on the physico-chemical properties of the seed oil indicates that the oil is semi-drying oil and may contain unsaturated fatty acids hence the oil could be a potential raw material for plastic formulation and protective coating industry. In this study, we have prepared metal soaps (cadmium, barium,zinc and calcium) using *H. crepitans* seed oil and examined their effect on the stabilization of UPVC against thermal degradation.

2. Materials and Methods

Uplasticised polyvinyl chloride used in this work is a homopolymer labeled as 0500M 40722bg and supplied by

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Oxyvinyls, Dallas, Texas, USA through KGM plastics Nigeria Ltd. Isolo, Lagos. All other chemicals and reagents used were of analytical grade or otherwise stated and were used as obtained without further purification.

2.1. Extraction and Characterization of Oil

The seed oil of *H. crepitans* was extracted in soxhlet apparatus using n-hexane and the physico-chemical properties were determined using standard methods as previously described [18]. The fatty acid methyl esters analysis was carried out using a Shimadzu QP 2010 plus GC–MS equipped with a HP-5 (30 m × 0.25 nm i.d., 5% dimethylsiloxane; film thickness, 0.25 μm) capillary column. Methyl esters were obtained by hydrolyzing the triglycerides of the oil with BF-methanol [19]. The column oven temperature was 70 ◦C with injection temperature of 250 ◦C. The column temperature was programmed from 70 ◦C to 280 ◦C where it was maintained for 5 min; helium was used as the carrier gas with inlet pressure of 100.1 kPa, linear gas velocity of about 45.4 cm/s, column flow rate: 1.53 ml/min. MS conditions were regulated as follows: ion source temperature: 200 ◦C, interface temperature: 250 ◦C, mass range: 30–350 amu. Fatty acids methyl esters were identified with individual standard and the quantification realized by area normalization.

2.2. Preparation of Metal Soaps of H. Crepitans Seed Oil

Metal soaps of *H* crepitans were prepared by methathesis in alcohol solution as previously described elsewhere [6]. The sodium soaps of the oil were first prepared by dissolving the oil sample (9.2g) in 50 mL of hot ethanol followed by treatment with 20 mL of 20 wt% sodium hydroxide solution. To this mixture 100 mL of 30 wt% solution of the metal salts were slowly added with continuous stirring. The precipitated metal soap was washed with hot water and dried in oven at 40 ^{o}C. The soaps were prepared using $BaCl_2.H_2O$, $CdSO_4$, $CaCl_2$ and $Zn(NO_3)_2$.

2.3. Preparation of UPVC Films

Varying weight percent (0, 5, 10, 15 and 20 wt %) of each of the metal soap was added to UPVC. A film of 50 μm thick was obtained by solvent casting in tetrahyhrofuran (THF). The films were extracted in vacuum to obtain films devoid of solvent [20]. UPVC films containing the additives in each case were obtained in a one pot process to avoid thickness variation.

2.4. Thermal Stability Study

Strips of film taken from different sections of the prepared UPVC films were conditioned in an Atlas Scorch Thermal Tester Oven at 180 ^{o}C and were removed at various time intervals and examined for colour change.

3. Results and Discussion

The physico-chemical properties of the seed oil of *H. crepitans* are given in Table 1. These properties especially the iodine value point to the fact that the oil is semi-drying oil and likely to contain unsaturated fatty acids which may be of industrial significance. The fatty acid compositions of the seed oil are listed in Table 2. The fatty acid profile reveals that the oil is predominated by linoleic acid (81.31%); the other constituents are palmitic acid (16.92%) and stearic acid (1.76%). The total saturated and unsaturated fatty acids in *H. crepitans* seed oil were found to be 18.68% and 81.31%, respectively. Its high linoleic acid content makes it particularly suitable for the manufacture of a range of protective coatings [21].

Table 1: Physico-chemical properties of *H. crepitans* seed oil

Assay	Value
Acid value	1.64
Saponification value (mg KOH/g oil)	210.38
Ester value (mg KOH/g oil)	208.74
Iodine value (mg KOH/g oil)	122.08
Peroxide value (meq/kg)	2.14
Unsaponifiable matter (%)	1.14
Specific gravity	0.91
Solidification point,(^{o}C)	−1− (−5)
PH (at 25 ^{o}C)	7.55

Table 2: Fatty acid composition of *H. crepitans* seed oil

Fatty acid	Value (%)
Palmitic acid	16.92
Linoleic acid	81.31
Stearic acid	1.76

Table 3 shows the effect of heat on UPVC films containing various compositions of the additives namely *H crepitans* seed oil, salt of lead ($PbCO_3$), metal soaps of cadmium, barium, zinc and calcium prepared using the seed oil at exposure time of 180 mins and at a temperature of 180 ^{o}C. From the table, it is seen that the UPVC that contain no additive was completely degraded confirming the thermal sensitivity of PVC and the need for stabilization against thermal degradation. Also the films containing *H. crepitans* seed oil degraded showing that the seed oil does not function as a stabilizer for the polymer.

Table 3: Thermal stability test on UPVC films containing various compositions of additives after 180 mins**.**

Composition (%)	0	5	10	15	20
UPVC + Oil	–	–	–	–	–
UPVC+ $PbCO_3$	–	+ +	+ +	+ +	+ +
UPVC + Cd Metal Soap	–	+	+ +	+ +	+ +
UPVC + Ba Metal Soap	–	+	+ +	+ +	+ +
UPVC + Zn Metal Soap	–	–	–	+	+ +
UPVC + Ca Metal Soap	–	–	–	+	+ +

Key: (−) = Colour change (+) = Slight colour change (+ +) = No colour change

It has been reported that basic lead salt is one of the best-known heat stabilizers for PVC [22]. On this basis, $PbCO_3$ was used as standard to compare the stabilizing ability of metal soaps of the metal used in this study. As could be seen in Table 3, films containing $PbCO_3$ showed no colour change at all the compositions. This shows that $PbCO_3$ exert a profound stabilizing effect on UPVC.

The UPVC films that contain Cd metal soap was slightly degraded as evident in the colour change at 5% composition Between 10 − 20 wt % composition, no colour change was observed. Similar trend was observed for UPVC films containing Ba metal soap. These results clearly show that the two additives (Cd and Ba metal soap) exert stabilizing effect on UPCV and compares favourably with basic lead salt. Results obtained also show that both Ca and Zn metal soaps did not stabilize UPVC film against thermal degradation between 5−10 wt % compositions as evident in the colour change of the films at these compositions. There was a slight colour change of the films that contain the additives at 15 wt % compositions while no colour change was noticed at 20 wt % compositions signifying that the two metal soaps only function as heat stabilizers at higher concentrations. The results obtained in this study especially for cadmium metal soaps corroborates earlier reports that cadmium soaps of carboxylic acids often exert synergistic stabilizing effect on the degradation of PVC [23, 24].

Stabilization action is achieved from some kind of interactions, the nature of which probably varies according to the type of stabilizers used. One possible stabilization action is the deactivation of labile sites responsible for initiating dehydrochlorination and it has been suggested that metal carboxylates and dialkyltin dicarbonate stabilizers function in this way. In some cases, it is also possible that stabilizers function by interaction with peroxide structure. It is known that organotin compounds analogous to PVC stabilizer react with hydroperoxide which may decompose to products which do not initiate degradative processes [25, 26]. Although the mechanism of stabilization of PVC against thermal degradation by the metal soaps used in this study is yet to be understood and subject to further investigation, it could be thought to be due to the replacement of labile chlorine atoms within UPVC structures with carboxylate groups which are more stable to heat as proposed by Frye and Horst [27, 28]. Direct evidence of chlorine substitution with carboxylate group was obtained from radioactivity studies [27] and more recently from FT-IR analysis of PVC/metal soaps films [6].

Results obtained from the study also show that the effectiveness of the metal soaps of *H crepitans* seed oil in stabilizing UPVC against thermal degradation was concentration dependent. The higher concentrations of the additives exhibited pronounced stabilizing effect in comparison to the lower concentrations.

4. Conclusions

H crepitans seed oil has some properties similar to some industrially established oils and may be a potential source of industrial oil. The metal soaps of cadmium, barium, zinc and calcium derived from the seed oil are effective in stabilizing UPVC against thermal degradation. This points to *H crepitans* seed oil additive as a potential raw material for plastic formulation and hence a step towards practical exploitation of this natural resource.

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