UTILISATION OF RUBBER SEED OIL IN THE STABILISATION OF POLYVINYL CHLORIDE AGAINST THERMAL DEGRADATION

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ABSTRACT

Thermal degradation studies on polyvinyl chloride in the presence of rubber seed oil, epoxidized rubber seed oil and metal soaps (barium, cadmium and lead) of the oils under oxidative and non-oxidative conditions were carried out at various temperatures. Changes in intrinsic viscosity and levels of unsaturation in the degraded polymer samples and kinetic data including the rate of dehydrochlorination at 1% degradation and the time required for degradation to attain 1% conversion were used to assess the effect of rubber seed oil and its derivatives on the susceptibility of the polymer to thermal degradation. It was found that although the values of the rate of dehydrochlorination were about the same order of magnitude (10^{-2}% min^{1}), the rates were relatively lower and the time at which degradation attained 1% conversion considerably higher in the presence of the additives than the corresponding values obtained in the absence of the additives. The data from solution viscosity measurements and from estimates of the number of double bonds formed in the degraded polymer indicated that metal soaps of rubber seed oil and of its epoxides exert a stabilising effect on the oxidative and non-oxidative degradation of polyvinyl chloride. Studies on the effect of mixtures of barium and cadmium soaps of rubber seed oil showed that the soap mixture containing 90wt% cadmium soap exerted marked synergistic stabilising effect on the degradation of polyvinyl chloride.

INTRODUCTION

The low thermal stability of polyvinyl chloride (PVC) is one of the inherent problems associated with the manufacture and use of the polymer. At elevated temperatures well below its decomposition temperature, PVC loses HCl and becomes discoloured, leading to changes in the chemical and physical properties of the polymer. 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 some authors[1-5] have claimed that these structural irregularities are responsible and can account for the low thermal stability of the polymer. Although structural defects considerably increase the initial rate of PVC degradation, it has been argued that on account of the low concentrations in normal PVC of these structural irregularities and of the difficulties in the identification and quantification of such small amounts of labile allylic and tertiary chlorides within normal PVC structure, that initiation of degradation of PVC also takes place at regular monomer units[6-8].

The poor thermal stability of PVC requires the use of stabilisers in the processing of the polymer. Additives that have found practical application as thermal stabilisers for PVC include metal salts of organic acids, organometallic compounds and inhibitors of radical chain reactions. In this study we examined the effects of the rubber seed oil, epoxidised rubber seed oil, and the metal soaps of the oils on oxidative and non-oxidative thermal degradation of PVC.

Rubber seed oil (RSO) is obtained from the seeds of the plant *Heavea brasiliensis* which is widely cultivated in the southern part of the country as an economic tree. At present, RSO has no commercial value in this country. The utilisation of RSO in the preparation of alkyd resins has been reported[9-12]

EXPERIMENTAL

Materials

Polyvinyl chloride (BDH) ($\bar{M}n$ 1.0 x 10^5; particle size 100% pass B.S. 60 mesh and 74% pass B.S. 200 mesh) was purified by dissolution in THF/acetone and precipitated, with constant stirring, in a large excess of methanol. The precipitated polymer was filtered off, washed with methanol and air-dried. RSO was obtained from the Rubber Research Institute of Nigeria, Benin. It was mechanically extracted from seeds collected over a period of one year. The physico-chemical characteristics and fatty acid profile of RSO[13] are shown in Table 1.

Epoxidation of rubber seed oil

Epoxidation of RSO was carried out at 29°C using peractic acid prepared *in situ* by reacting hydrogen peroxide (30% v/v) with excess glacial acetic acid. The level of epoxidation was determined using the method described by Durbetaki[14]. The epoxidised rubber seed oil (ERSO) was stored at 7°C until required.

Table 1: Physico-chemical characteristics and fatty acid composition of rubber seed oil.

Characteristics	Values
Specific gravity (at 30°C)	0.926
Free fatty acid(%) (as oleic acid)	11.29
Acid value (mgKOH/g)	23.00
Peroxide value (meq/kg)	0.40
Iodine value (mgI_2/100g)	155.56
Saponification value (mgKOH/g)	201.46
% fatty acid composition:	
Myristic acid	2.2
Palmitic acid	7.6
Stearic acid	10.7
Oleic acid	20.0
Linoleic acid	36.0
Linoleinic acid	23.5

Preparation of metal soaps of rubber seed oil

Metal soaps were prepared from RSO and ERSO by metathesis in alcohol solution[15,16]. The sodium soaps of the oils were first prepared by dissolving the oil sample (9.2g) in 50ml of hot ethanol followed by treatment with 20ml of 20wt% sodium hydroxide solution. To this mixture 100ml of 30wt%

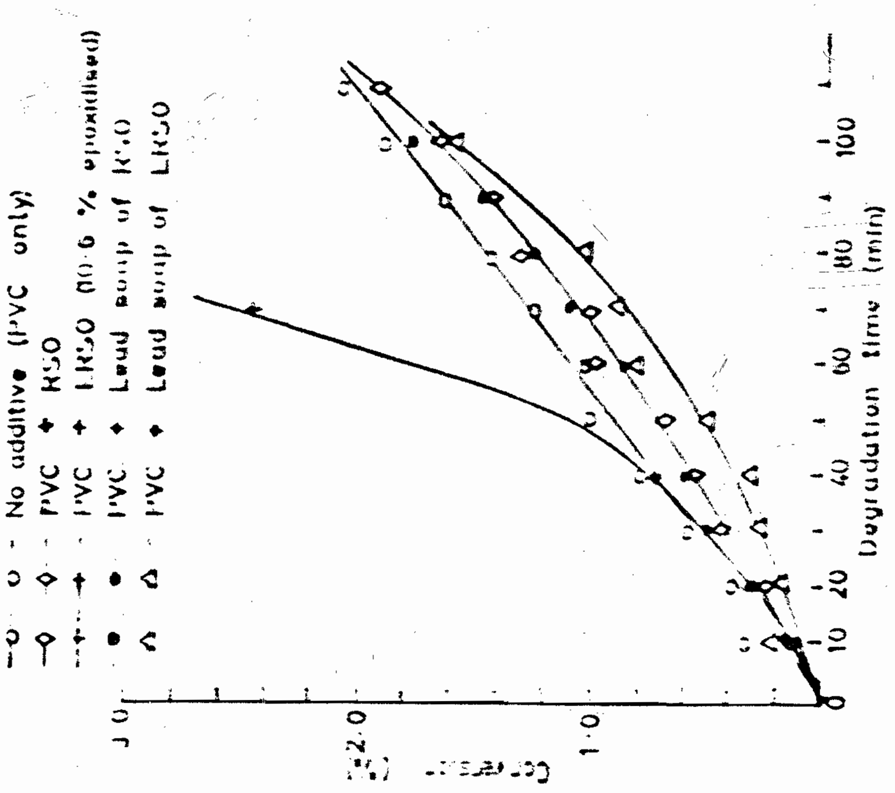
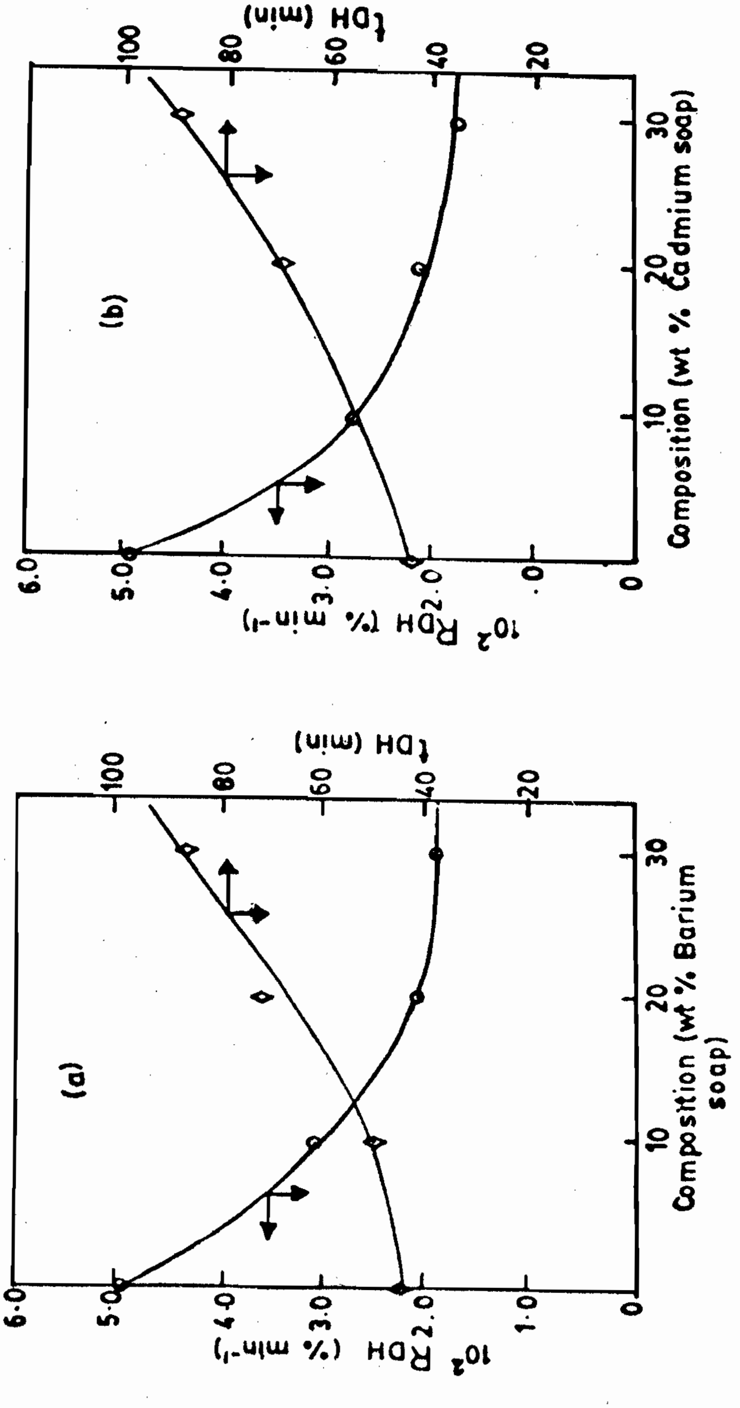


Fig. 1. Dehydrochlorination of PVC at 190°C in the presence of Rubber seed oil additives

Fig. 2: Thermal Degradation of PVC at 190°C in the presence of mixtures of Epoxidised Rubber seed oil and metal soaps of the oil; (a) Effect of barium soap and (b) Effect of cadmium soap.

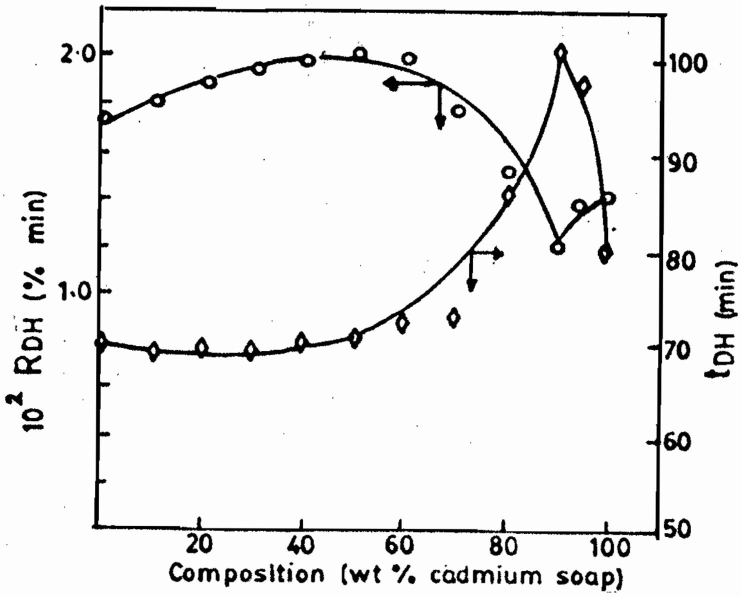


solution of the metal salts were slowly added with continuous stirring. The precipitated metal soap was washed with hot water and air-dried. The soaps were prepared using $BaCl_2.2H_2O$; $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$.

Non-oxidative degradation: rates of dehydrochlorination

In the non-oxidative dehydrochlorination studies, 1.5g of PVC was mixed thoroughly, one at a time, with 10 wt% of RSO or ERSO or 3 wt% of the metal soaps of the oils and the mixture was transferred to a degradation tube. The tube was connected

Fig. 3: Dehydrochlorination of PVC at 190°C in the presence of mixtures of barium and cadmium soaps of RSO



to a source of nitrogen maintained at a flow rate of 60ml min^{-1}. The degradation tube was immersed in a thermostated oil bath controlled to better than ± 1°C. The HCl evolved was passed into a known volume of 0.01M sodium hydroxide solution. The amount of HCl evolved after various periods of time was established by titration with 0.01M HCl solution. The extent of dehydrochlorination (%) was calculated from the ratio of HCl evolved to the amount available in the polymer. Degradation was carried out at 170, 180 and 190°C. The values of the rates of dehydrochlorination at 1% conversion, R_{DH}, and the time required for degradation to attain 1% conversion, t_{DH}, for non - oxidative degradation of PVC in the presence of RSO-based additives are shown in Table 2. The rates of dehydrochlorination of PVC at 190°C in the presence of RSO, ERSO and barium soap of the oils are shown in Fig. 1.

Non-oxidative degradation studies on PVC in the presence of mixtures of (a) RSO epoxidised to 10.6mol % and metal soaps of RSO and (b) barium and cadmium soaps of RSO were carried out at 190°C. The results are shown in Figs. 2 and 3 respectively.

Oxidative degradation

Thermoxidative studies were carried out in air as decribed for non-oxidative degradation except that rates of dehydrochlorination were not monitored. Degradation was allowed to proceed for 30, 60 and 90 min respectively at the end of which the degradation tube was allowed to cool and the degraded polymer was recovered and stored in the dark. Thermoxidative degradation studies on PVC were also carried out at 190°C using mixtures of barium and cadmium soaps of RSO. The variations of the relative intrinsic viscosity $[\eta]/[\eta]_o$ and of iodine values, IV/IV_o, of the degraded PVC samples are shown in Figs. 4 and 5 respectively as a function of composition of the soap mixture.

Viscosity measurements

A portion of the degraded polymer sample was dissolved in cyclohexanone and precipitated in a large excess of methanol. Viscosity measurements of undegraded and degraded PVC samples were carried out in cyclohexanone solution at 30°C. The intrinsic viscosities and Huggin's interaction constant were determined using the relationship[17].

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \;.\;.\;.\;.$$

Here η_{sp} is specific viscosity measured as $(\eta_{rel} - 1)$, where η_{rel} is given by $\eta/\eta_s \approx t/t_o$ and η is the viscosity of the polymer solution and η_s is the viscosity of the solvent measured at the same temperature. t is the flow time of the polymer solution and t_o is the flow time of the solvent. $[\eta]$ and k are the intrinsic viscosity and Huggin's constant respectively and C is the concentration of the polymer solution in g/dl.

The ratio of intrinsic viscosity of PVC samples degraded in the presence of RSO additives to the viscosity of undegraded sample ($[\eta]/[\eta]_o$) were used to deduce the effect of the additives on the degradation of PVC (Table 3).

Table 2: Dehydrochlorination rate data for PVC in the presence of rubber seed oil derivatives

Additive	Temp.(°C)	t_{DH} (min.)	10^2 R_{DH} (%min^{-1})
None	170	86	1.11
	180	55	1.73
	190	35	2.78
RSO	170	90	2.16
	180	50	2.67
	190	30	4.29
ERSO			
4.8% epoxidation	170	116	2.00
	180	75	3.60
	190	40	5.83
9.2% epoxidation	170		
	180	90	3.10
	190	42	5.33
10.6% epoxidation	170		
	180	92	2.75
	190	44	5.00
Metal soaps of RSO(ERSO)			
Barium soap	170		
	180	112	1.54
	190	60(70)	2.31(2.17)
Cadium soap	170		
	180	116	1.60
	190	63(75)	
Lead soap	170		
	180	113	1.54
	190	77(80)	1.78(2.17)
Metal soaps of oleic acid(linoleic acid)			
Barium soap	190	56(65)	2.13(2.20)
Cadmium soap	190	56(65)	2.00(2.20)
Lead soap	190	67(65)	1.95(1.89)

Levels of unsaturation in polymer samples

The levels of unsaturation in the PVC sample were estimated from their iodine values determined by the Wij's method[18]. The results are shown in Table 4.

RESULTS AND DISCUSSION

Non-oxidative degradation: rates of dehydrochlorination

The rates of dehydrochlorination of PVC at 170 and 180°C in the presence of RSO - based additives are similar to the plots in Fig. 1. It can be seen from the results in Fig. 1 that although no initial induction periods are observed, the initial rates of evolution of HCl, in the presence of the additives, were generally relatively low and gradually increased after about 40 min of degradation. The occurrence of a period of

Table 3: Viscosity parameters for PVC degraded at 190°C in the presence of rubber seed oil additives

Additive	Period of degradation (min)	Intrinsic viscosity$[\eta]$ (dl/g)	Huggin's constant k	Relative intrinsic viscosity $[\eta]/[\eta]_o$
None	30	0.45	35.70	0.41
	60	0.36	39.54	0.33
	90	0.24	86.50	0.22
RSO	30	0.67	18.80	0.61
	60	0.40	42.25	0.36
	90	0.30	77.44	0.27
ERSO				
4.8% epoxidation	30	0.72	14.42	0.65
	60	0.41	38.65	0.37
	90	0.30	53.75	0.32
10.6% epoxidation	30	0.81	12.35	0.74
	60	0.52	25.07	0.47
	90	0.38	49.79	0.35
Metal soaps of RSO(ERSO)				
Barium soap	30	0.80(0.90)	12.59(8.11)	0.73(0.82)
	60	0.64(0.64)	16.88(16.88)	0.58(0.58)
	90	0.48(0.48)	32.61(32.96)	0.44(0.44)
Cadium soap	30	0.69(0.90)	17.85(8.64)	0.63(0.82)
	60	0.57(0.59)	21.88(21.63)	0.52(0.54)
	90	0.46(0.46)	34.90(34.62)	0.42(0.42)
Lead soap	30	1.00(0.99)	6.88(7.02)	0.91(0.90)
	60	0.68(0.72)	14.78(13.27)	0.62(0.65)
	90	0.58(0.58)	20.24(20.29)	0.53(0.53)

$[\eta]_o = 1.10$ $k_o = 5.40$

retarded loss of HCl is indicative of a stabilising influence on the degradation process.

The rates of dehydrochlorination of PVC in the presence of RSO at 170, 180 and 190°C at 1% degradation were about the same order of magnitude (10^{-2}% min^{-1}) being highest at 190°C (R_{DH} 4.29% min^{-1}). The values of t_{DH} ranged from 30 min at 190°C to 90min at 170°C. When compared with values obtained for degradation in the absence of RSO, these results indicate that RSO has deleterious effect on the stability of PVC; reducing t_{DH} by as much as 5 min and increasing the R_{DH} value as much as nearly two-fold (Table 2). Rubber seed oil consists of glyceryl esters of fatty acids or triglycerides and small amounts of soluble impurities such as pigments, vitamins, sterols, phospholipids, glycolipids and traces of hydrocarbons and ketones[19]. The level of unsaturation in the hydrocarbon chain of the fatty acid makes it difficult to obtain RSO in a high state of purity, particularly traces of oxidation products, promoted by free atmospheric oxygen and traces of metals such as copper and iron[20] occur.

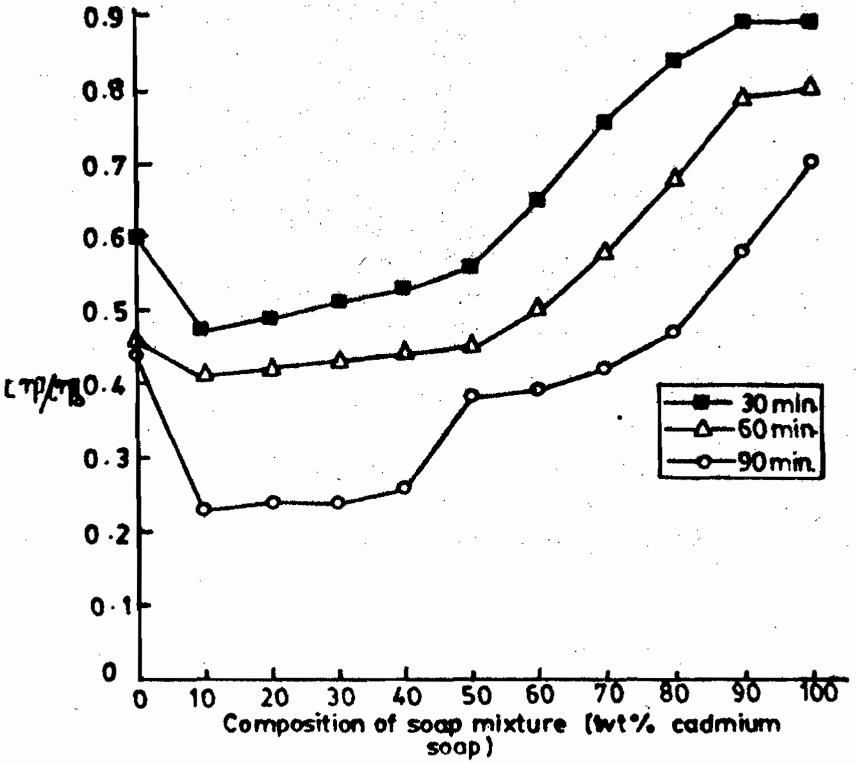


Fig. 4 Thermoxidative degradation of PVC in the presence of mixtures of barium and cadmium soaps of RSO at 190°C. Variation of relative intrinsic viscosity with composition of soap mixture.

Autoxidation of oil involves various steps which include the formation and subsequent decomposition of hydroperoxide. It is thought that the presence of radicals and products of hydroperoxide decomposition could accentuate HCl evolution from PVC since it is generally well accepted that dehydrochlorination of PVC is enhanced by free radicals[21]; this could explain the apparent high rates of dehydrochlorination of PVC in the presence of RSO.

The results for ERSO (Table 2) show that the values of t_{DH} increase from 116min to 120min at 170°C, 75min to 92min at 180°C and from 40min to 44min at 190°C as the level of epoxidation increased from 4.8% to 10.6%. The values of R_{DH} decreased with increase in the levels of epoxidation of RSO. The results show that in the presence of ERSO, the R_{DH} values are higher than the values obtained with RSO and without the additives, suggesting that ERSO has a deleterious effect on the thermal degradation of PVC. However, the values of t_{DH} obtained in the presence of ERSO are relatively higher than the corresponding values for RSO and in the absence of the additives indicating retardation of the decomposition of PVC and a stabilising effect. The stabilising effect of ERSO on the thermal degradation of PVC is considered to result from the facile reaction of HCl with epoxy group to form chlorohydrin, which is considered to reduce the autocatalytic effect of the HCl evolved at the initial stages of dehydrochlorination on the degradation process. The effectiveness of stabilisation should depend on the epoxy content of the additive and on the stability to heat of the additive and the chlorohydrin formed by the reaction with HCl. The results from this study show that ERSO exhibits some stabilising influence on the thermal degradation of PVC at the early stages of degradation (below 1% conversion) and that the values of R_{DH} suggest that ERSO and/or

Table 4: Levels of unsaturation of PVC samples degraded at 190°C in the presence of rubber seed oil additives for 60 min.

Additive	Iodine value (IV) (mgI_2/100g sample)	Relative Iodine Value $(IV)/(IV)_o$
None	180.56	19.01
RSO (10wt%)	161.50	17.01
ERSO (10wt%)		
4.6% epoxidised	171.06	18.01
10.6% epoxidised	142.55	15.01
Metal soaps of RSO (3wt%)		
Barium soap	114.04	12.00
Cadmium soap	104.54	11.00
Lead soap	85.53	9.00

$IV_o = 9.50$

its derived chlorohydrin may not be heat-stable.

The results in Table 2 also show that the metal soaps of RSO are more effective than RSO and ERSO in suppressing dehydrochlorination of PVC and that the order of increasing stabilisation effectiveness is barium soap < lead soap < cadmium soap. The mechanism by which metal soaps stabilise PVC against thermal degradation was first proposed by Frye and Horst[22,23] and it involves the replacement of labile chlorine atoms within PVC structure with carboxylate groups which are more stable to heat treatment. Direct evidence of chlorine substitution with carboxylate group was obtained from radioactivity retention studies[22] and more recently from FT-IR analysis of PVC/metal soap films[24]. The enhanced stabilisation effectiveness of the metal soaps from RSO is thought to be due to the higher heat stability of the soaps than ERSO and RSO[24]. The values of R_{DH} and t_{DH} obtained for degradation of PVC in the presence of metal soaps of ERSO are shown in Table 2. The valus of t_{DH} and R_{DH} obtained in the presence of the metal soaps of ERSO are more than 50% higher and 50% lower respectively than the corresponding values obtained in the presence of ERSO. The results also indicate that the metal soaps of ERSO are relatively more effective than the soaps of RSO in stabilising PVC against thermal degradation. It is thought that the metal soaps of ERSO showed the combined effects of the epoxy group and the metal soap in stabilising PVC against thermal degradation. The values of t_{DH} and R_{DH} for the degradation of PVC at 190°C in the presence of mixtures of RSO epoxidised to 10.6mol% and the metal soaps are shown in Fig. 2. It can be seen that the values of t_{DH} in the presence of the mixtures increase from 50min to 86min (72% increase) as the barium soap content of the mixture was increased from 10 to 30wt%, while an increase in the value of t_{DH} of 68% was observed for a similar increase in the cadmium soap content of the mixture. A decrease in the values of R_{DH} from $3.14 \times 10^{-2}\%\ min^{-1}$ to $1.9 \times 10^{-2}\%$ for mixtures containing barium soap and from $2.8 \times 10^{-2}\%\ min^{-1}$ to $1.7 \times 10^{-2}\%\ min^{-1}$ for mixtures

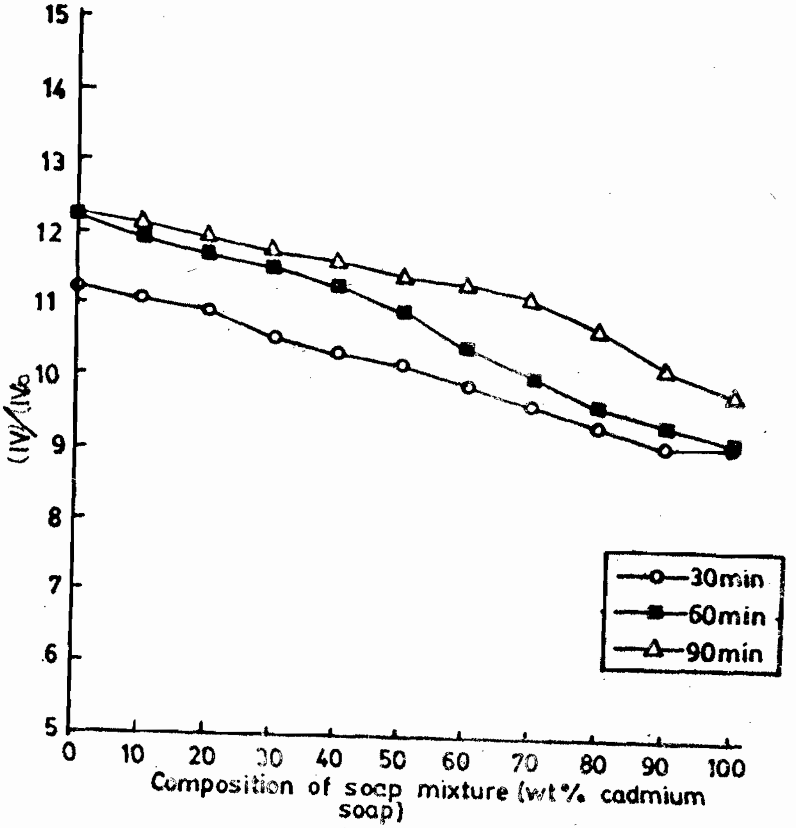


Fig. 5 Thermoxidative degradation of PVC in the presence of mixtures of barium and cadmium soaps of RSO at 190°C Variation of iodine value of degraded samples with composition of soap mixture.

containing cadmium soaps was obtained within the range of composition of ERSO/metal soap mixture studied. When compared with the values obtained for the degradation of PVC in the presence of metal soaps of ERSO, these results show that blending ERSO and metal soaps of RSO will enhance the thermal stabilisation effectiveness of the additives.

Barium and cadmium soaps of carboxylic acids are often reported to exert synergistic stabilising effect on the degradation of PVC[25,26]. The results in Fig. 3 show that the effect of binary mixtures of barium and cadmium soaps of RSO on the degradation of PVC is not additive. The values of R_{DH} increased to a maximum value of about 2.0% min^{-1} at 50wt % cadmium soap content of the mixture and thereafter decreased to a minimum value of 1.23% min^{-1} at 90wt % cadmium soap content of the mixture. The values of t_{DH}, on the other hand, increased with increase in the cadmium soap content of the mixture, with the highest value of 101min at 90 wt% cadmium content of the mixture. When compared with the values obtained using single soaps of RSO, these results show that the mixtures of barium and cadmium soaps of RSO exhibited antagonistic effect with soap mixtures containing less than 60wt % cadmium soap and synergistic effect at higher cadmium soap content of the mixture. A reaction sequence has been described[25,26]. It would appear from the results in Fig. 3 that the reaction sequence attained optimum effectiveness at cadmium soap to barium soap ratio of 9:1.

The main fatty acid components of RSO are oleic acid and linoleic acid (Table 1). It was thought that the effect of the metal soaps of these acids on the thermal degradation of PVC would approximate the effect of the metal soap of the oil and would allow an assessment of the contribution of the hydrocarbon (unsaturated) moiety to the

Table 5: Thermooxidative degradation of PVC at 190°C in the presence of metal soaps of RSO

Additive	Period of Degradation (min)	Huggin's constant k	Intrinsic viscosity $[\eta]$ (dl/g)	Relative intrinsic viscosity $[\eta]/[\eta]_o$	Iodine value(IV) mgI$_2$/100g sample	Relative Iodine value $(IV/IV)_o$
None	30	23.14	0.59	0.31	174.63	17.83
	60	17.64	0.60	0.32	180.20	18.39
	90	54.33	0.38	0.20	184.20	18.80
Barium soap of RSO	30	7.12	1.14	0.60	110.20	11.25
	60	9.94	0.88	0.46	119.75	12.22
	90	5.68	0.84	0.44	120.16	12.26
Cadmium soap of RSO	30	2.03	1.70	0.89	88.93	9.08
	60	3.80	1.50	0.80	89.90	9.17
	90	2.83	1.33	0.70	96.30	9.83
Lead soap of RSO	30	2.84	1.52	0.80	100.06	10.21
	60	4.13	1.34	0.71	100.34	10.24
	90	4.45	1.17	0.62	106.85	10.90

stabilising effect of the soap to be made. The values of R_{DH} and t_{DH} obtained for PVC degraded in the presence of barium and cadmium soaps of oleic and linoleic acids are shown in Table 2. The values of R_{DH} varied from 2.13 x 10^{-2} % min^{-1} for PVC stabilised with barium soap of oleic acid to 1.95 x 10^{-2} % min^{-1} for the PVC stabilised with the lead soap while the values of t_{DH} varied from 56 min to 67 min for barium oleate and lead oleate stabilised PVC samples respectively. It can be seen from the values of R_{DH} and t_{DH} that the soaps of linoleic acid tend to be less effective than the soaps of oleic acid in stabilising PVC against thermal degradation. The hydrocarbon portion of a metal carboxylate may influence stability by altering polymer-matrix polarity, although the exact nature of this effect is yet not fully understood[27]. Oleic acid and linoleic acid are both C_{18} unsaturated fatty acids, with the latter acid having two double bonds against the single bond in oleic acid. It is thought that the higher level of unsaturation in linoleic acid may account for the reduced effectiveness of its soaps in stabilising PVC against thermal degradation. The results also show that the soaps of oleic and linoleic acids are relatively less effective stabilisers than the soaps of RSO. Rubber seed oil contains 20% saturated acids and about 80% unsaturated fatty acids. The observed difference between the stabilisation effectiveness of the metal soaps of RSO and soaps of oleic and linoleic acids is an indication of the contribution of the chemical identity of the hydrocarbon moiety of the soaps to the overall stabilisation process.

Viscosity measurements

It has been reported that the intrinsic viscosity of PVC undergoing degradation decreases initially to a minimum and then increases with further increase in the number of conjugated double bonds in the polymer[28], probably due to reduced flexibility along the main polymer chain axis and cross-linking. Therefore, if the extent of dehydrochlorination is kept low, changes in the values of intrinsic viscosity can be taken as estimates of the extent of degradation: the lower the value of instrinsic viscosity, the greater the extent of degradation. The relative intrinsic viscosity, $[\eta]/[\eta]_o$, where $[\eta]_o$ is the intrinsic viscosity of undergraded PVC sample, can be used to assess the extent of degradation and the effect of RSO derivatives on the degradation process. It can be seen from the results in Table 3 that the values of $[\eta]/[\eta]_o$ are highest for PVC samples stabilised with metal soaps of ERSO and lowest for the unstabilised PVC samples. These results show that RSO additives are relatively effective in stabilising PVC against thermal degradation.

Level of unsaturation in degraded PVC samples

The evolution of HCl during thermal degradation of PVC leads to the formation of olefinic bonds in the polymer molecule. Therefore, if the extent of degradation is low and dehydrochlorination is not accompanied by secondary reactions, measurement of the level of unsaturation in the degraded polymer sample should provide an estimate of the extent of degradation. The results in Table 4 show that the iodine values varied from 9.50 for undegraded PVC to 180.56 for the unstabilised PVC sample degraded at 190°C. The iodine values for degraded PVC samples containing RSO additives varied from 171.06 for PVC stabilised with ERSO (with 4.8% epoxide content) to 85.53 for PVC stabilised with lead soap of RSO. These results represent a decrease of between 5.25% and 52.63% in iodine value relative to the value obtained for unstabilised PVC. The iodine value (161.55) obtained for PVC samples stabilised with RSO is lower, by as much as 19.01 iodine value units, than the corresponding value for the unstabilised PVC. The ratio of the iodine value of degraded PVC sample to the value of undegraded sample, IV/IV$_0$, can be used to assess the relative effect of the RSO additives on the thermal degradation of PVC. The values of relative iodine values, IV/IV$_0$, varied from 19.01 for unstabilised PVC to 9.0 for PVC stabilised with lead soap of RSO. The results in Table 4 clearly show that the addition of RSO to PVC reduces the levels of unsaturation in the degraded polymer samples 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 various periods of time in the presence of RSO additives are shown in Table 5. The results show that the values of intrinsic viscosity of the degraded PVC samples are markedly lower than the value for the undegraded sample It can be seen from the results in Table 5 that whereas the value of intrinsic viscosity of the PVC sample degraded without the additives is only 30% of the value of the undegraded sample, the values of intrinsic viscosity of PVC samples degraded in the presence of the metal soaps of RSO are much higher, with values of between 60 and 90% of the value of the undegraded sample. 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 Huggin's constant is generally used as a measure of the polymer-solvent and polymer-polymer interaction. In conjuction with intrinsic viscosity values, the Huggin's constant, being indicative of variations in intermolecular forces, can give an overall view of macromolecular configuration and behaviour in solution.

It can be seen that the relative iodine value, IV/IV$_0$ varied from about 18.0 for unstabilised PVC to about 9.0 for PVC stabilised with cadmium soap of RSO. These results show that metal soaps of RSO are effective in stabilising PVC against thermoxidative degradation.

It can be seen from the results in Fig. 4 that the initial decrease in the values of relative intrinsic viscosity at low cadmium soap content of the binary soap mixture is followed with increase in relative intrinsic viscosity values at higher cadmium soap content of the mixture. These results show that the effect of mixed barium and cadmium soaps of RSO on the degradation of PVC is not additive showing antagonistic effect of mixture composition up to about

60wt% cadmium soap and synergistic effect at higher cadmium soap content of the mixture; this is similar to the trend observed for non-oxidative degradation. Fig. 5 shows the variation in the IV/IV_0 values as a function of the composition of the soap mixture. The results show that the stabilising effect of barium soap is enhanced by the presence of cadmium soap throughout the entire composition range.

CONCLUSION

The data obtained from this study are corroborative and show that the derivatives of RSO studied are effective in stabilising PVC against thermal degradation. The suggested potential application of RSO additives as thermal stabilisers in PVC formulations is an important first step to fuller exploitation of the resources of the rubber tree.

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accepted 30/7/99

received 4/5/99