Thermal Stabilization of Poly(vinyl chloride) by Metal Carboxylates of *Ximenia americana* Seed Oil Under Inert Condition

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Abstract

The kinetics of thermal degradation of poly(vinyl chloride), (PVC) in the presence of lead, cadmium, barium, calcium and zinc soaps of *Ximenia americana* seed oil (XSO) was investigated under nitrogen atmosphere in the temperature range, 170-190°C. The stabilizing effects of the metal soaps were assessed by measurements of the time for degradation to attain 1% conversion, t_{DH} and of the corresponding rate of degradation, R_{DH}. PVC was stabilized by the metal soaps with exception of the zinc derivative, and showed a relative order of stabilization of PbXSO>BaXSO>CaXSO>CdXSO. The latter was corroborated by measurements of intrinsic viscosity of degraded PVC samples and thermogravimetric analysis. The zinc soap accentuated the degradation of PVC at a rate 5-fold higher than the value in the absence of additive at 190 ^{o}C. The calculated activation energies for the degradation process are in the range 79.76 – 85.3 kJmol^{-1} for PVC alone and PVC/Ba-XSO composition. Binary mixtures of Ca/Zn and Ba/Cd carboxylates both at 9:1 ratio exhibited synergistic effect on PVC stabilization.

Keywords: Poly(vinyl chloride), *Ximenia americana*, thermal stabilization, metal soaps, degradation

1. Introduction

Without the discovery of thermal stabilizers, poly(vinyl chloride), PVC would have remained commercially unimportant polymer due to the fact that it degrades at elevated temperatures. However, it is one of the leading commercial polymers due to its versatility, thanks to the discovery of thermal stabilizers. Processing of PVC to useful materials takes place above160 ^{o}C, a temperature much higher than its glass transition temperature (70 ^{o}C) [1]. The degradation of PVC occurs via thermal dehydrochlorination leading to the release of hydrogen chloride gas (HCl) and the formation of conjugated double bonds in the polymer chain [2]. This results in severe colouration and loss of physical and mechanical properties [3, 4]. Thermal degradation of PVC is autocatalytic as the process is accelerated by the released HCl and its poor thermal stability requires the use of thermal stabilizers during processing [5]. The thermal stabilizers function by absorbing the released HCl and/or substitution of labile groups in the PVC macromolecules [6] thereby preventing dehydrochlorination. Various types of thermal stabilizers have been employed in PVC processing; however, metal carboxylates have played a major role in the development of PVC as an important commercial polymer [7]. The bulk of these metal carboxylates were prepared from pure fatty acids. Recent studies [2, 8, 9, 10, 11] have shown that these carboxylates could be prepared from triglycerides and are thermally stable within the temperature range employed in the processing of PVC. Similarly, our earlier report [7] revealed that metal carboxylates of *Ximenia americana* and *Balanites aegyptiaca* seed oils are thermally stable within the temperature range for processing PVC. The aim of this work is to investigate thermal stabilizing effects of metal carboxylates of *Ximenia americana* seed oil (XSO) on PVC so as to add commercial value to this oil that has no commercial value in Nigeria presently.

2. Experimental

Materials and Methods

Poly(vinyl chloride), obtained from Sigma-Aldrich Co (USA) (Mn, 0.9 x 10^5) was purified as reported earlier [12]. The metal carboxylates were prepared as earlier reported [7]. Thermal degradation of PVC was carried out in the presence of the metal carboxylates in the temperature range 170 ^{o}C to 190 ^{o}C under nitrogen atmosphere as earlier described[12]. For viscosity measurements, the degraded PVC samples were purified by solution in cyclohexanone and precipitation in methanol. The precipitated polymers were filtered off and air-dried. Dilute solution viscosity measurements of undegraded and degraded samples were carried out in cyclohexanone using Ubbelohde capillary viscometer, mounted in a thermo stated water bath at 30±0.1^{o}C. The intrinsic viscosity, [η] was determined from the Huggins equation:

$$\eta/C = [\eta] + K'[\eta]^2 C$$

The stabilizing effects of the metal soaps were evaluated from the ratios of the intrinsic viscosity of PVC samples degraded in the presence of additives, [η] to the viscosity of undegraded sample, $[\eta]_0$ i.e., $[\eta]/[\eta]_0$. Fourier-transform infra-red (FT-IR) spectrophotometric studies on the interactions of metal carboxylates with PVC in PVC film were conducted using Nicolet Avatar 330FT-IR spectrophotometer.

Thermogravimetric study of PVC degradation in the presence of the metal carboxylates was conducted using Perkin-Elmer Pyris 6 thermal gravimetric analyzer programmed at a heating rate of 10 ^{o}C min^{-1} up to a temperature of 550 ^{o}C under nitrogen.

3. Results and Discussion

Figure 1 shows the conversions in PVC degradation under nitrogen at 190 ^{o}C in the presence of 3 wt% metal carboxylates of XSO. The effect of the metal soaps was evaluated from the time for degradation to attain 1% conversion, t_{DH} and the corresponding rate of degradation at 1% conversion, R_{DH}. The results are presented in Table I. In the absence of additives, t_{DH} and R_{DH} values for PVC degradation increase with temperature in the range, 170-190 ^{o}C. At 190 ^{o}C, t_{DH} and R_{DH} are 34 min and 3.0 x 10^{-2} %min^{-1} respectively. In the presence of 3 wt% Zn-XSO, the degradation of PVC at 180 and 190 ^{o}C is accentuated having t_{DH} and R_{DH} values of 16min and 16.0 x 10^{-2} %min^{-1} respectively at the latter temperature. Thus, the rate of degradation of PVC at 190 ^{o}C in the presence of Zn-XSO is 5-fold higher than the corresponding one in the absence of additives. This is in contrast to a reported stabilizing effect of the zinc soap of khaya seed oil on PVC at this temperature [13]. For the other soaps, namely Cd-XSO, Pb-XSO, Ba-XSO and Ca-XSO, there is marked stabilizing effect on PVC degradation under nitrogen conditions. The order of stabilization of PVC by the metal soaps is:

Pb-XSO > Ba-XSO > Ca-XSO > Cd-XSO.

The mechanism of stabilization of PVC by metal soaps is generally believed to involve replacement of labile chlorine atoms by heat-stable carboxylate groups. In addition, it has been shown that the mechanism for stabilization of PVC by seed oils involves HCl trapping by unsaturated fatty acid moieties through addition reactions [12]. Thus, for metal soaps, the mechanism of stabilization of PVC is composite consisting of HCl trapping reactions and substitution of labile chlorine atoms by carboxylate groups. Consequently, under equivalent concentrations, the metal soaps are expected to be more effective stabilizers of PVC than the native oil. This is corroborated by the t_{DH} (76min) and R_{DH} (2.02 x 10^{-2} %min^{-1}) for Pb-XSO at 190 ^{o}C which are 55% higher and 19% lower respectively than the corresponding values for XSO i.e., 49min and 2.50 x10^{-2} %min^{-1}. The order of stabilization of PVC by the metal soaps of XSO, shown above, is supported partly from studies on the metal soaps of khaya seed oil [13] and rubber seed oil [14]. However, for jatropha seed oil, the order with respect to cadmium and barium is reversed i.e., cadmium soap exerted a higher stabilizing effect on PVC than the barium soap. Thus, it may be deduced that for different seed oils, the order of stabilization of PVC by the metal soap derivatives is a function of the intrinsic aggregate chemical properties leteof their fatty acid constituents.
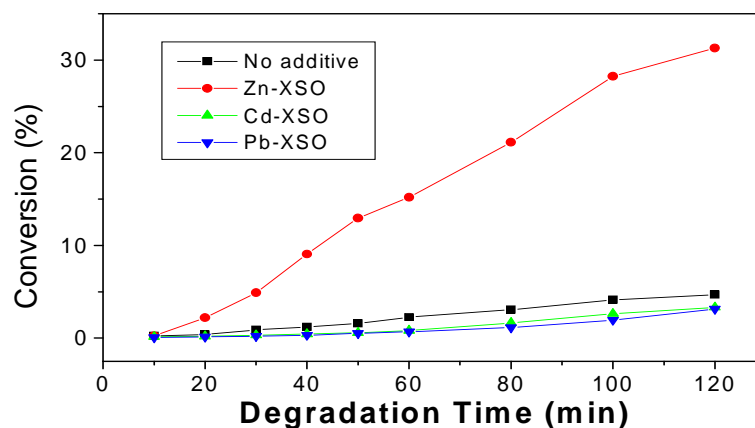
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Figure 1: Effect of 3 wt% metal carboxylates of XSO on PVC degradation at 190 ^{o}C under N_2.

Table 1. Kinetic parameters for dehydrochlorination of PVC under nitrogen in the presence of metal carboxylates of XSO

Additive, 3wt-%	Temperature ^{o}C	t_{DH} min	$10^2 R_{DH}$ %min^{-1}	Rate Constant k_1, min^{-1}
None	170	78	1.76	1.10
	180	56	1.90	1.19
	190	34	3.00	1.88
Zn-XSO	180	48	10.0	6.25
	190	16	16.0	10.0
Cd-XSO	180	103	1.82	1.14
	190	61	2.92	1.83
Pb-XSO	180	>120		
	190	76	2.02	1.26
Ba-XSO	180	107	1.35	0.84
	190	74	2.19	1.37
Ca-XSO	190	65	2.50	1.56

From the rate constants for degradation of PVC, k_1 in Table I, the calculated activation energies for the process are shown in Table 2.

Table 2. Activation energy parameters for thermal degradation of PVC under nitrogen in the presence of metal carboxylates of XSO

Additive, 3wt-%	Activation Energy kJmol^{-1}
None	79.76
Zn-XSO	81.97
Cd-XSO	82.54
Ba-XSO	85.31

The activation energy values are consistent with the order of stabilization of PVC based on t_{DH} and R_{DH} values. The activation energy value of 81.97 kJmol^{-1} in the presence of Zn-XSO is close to the one for PVC in the absence of additives. However, it is to be noted that activation energy for degradation of PVC is

dependent on a number of factors, namely, variation in the molecular weight and molecular weight distribution of the polymer; the polymerization processes; the nature and amount of impurities in the polymer and the experimental conditions.

Figure 2 shows the plots of relative intrinsic viscosity $[\eta]/[\eta]_0$ versus degradation time for PVC stabilized by 3 wt% metal soaps of XSO at 190 ^{o}C under nitrogen. The collected values are shown in Table 3.
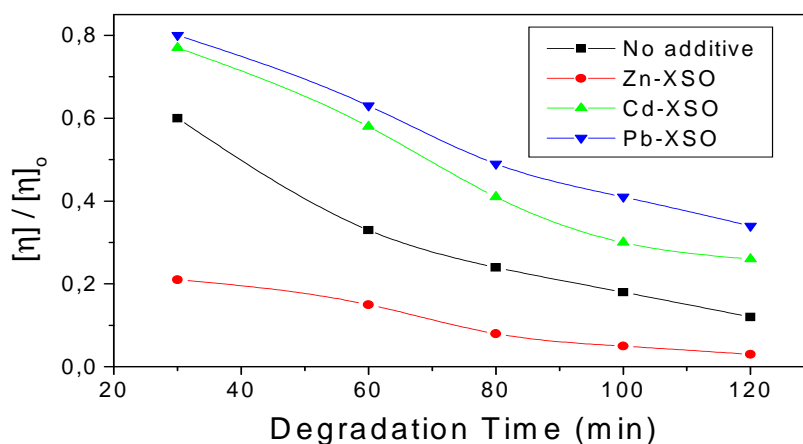

Figure 2: Plots of relative intrinsic viscosity vs degradation time for PVC stabilized by 3 wt% metal carboxylates of XSO at 190 ^{o}C under N$_2$.

Table 3. Intrinsic viscosity of PVC after degradation at 190°C under nitrogen in the presence of barium and calcium carboxylates of XSO.

Additive, 3wt-%	Degradation time min	$[\eta]$ dl/g	$[\eta]/[\eta]_o$
BaXSO	30	1.22	0.78
	60	0.94	0.60
	80	0.71	0.46
	100	0.59	0.38
	120	0.48	0.31
CaXSO	30	1.22	0.78
	60	0.93	0.59
	80	0.68	0.44
	100	0.54	0.35
	120	0.43	0.28

$[\eta]_o$ is the intrinsic viscosity of undegraded polymer and $[\eta]$, the value after varying degradation time. The non-oxidative degradation of PVC is believed to be characterized by three types of reaction, namely, dehydrochlorination, chain scission and cross linking, the later reaction having the tendency to increase the viscosity of the polymer. In Figure 2, it can be seen that the relative intrinsic viscosity decreases with increase in degradation time. The deleterious effect of Zn-XSO on degradation of PVC is evident having $[\eta]/[\eta]_o$ value at 120min which is 75% lower than the corresponding value for PVC without additive. The other metal soaps show considerable stabilization of PVC as can be seen in Figure 2. Typically, for Cd-XSO, the least stabilizing of the soaps, the value for $[\eta]/[\eta]_o$ at 120min degradation time is 116% higher than the corresponding value in the absence of additive. The order of stabilization of PVC by the metal soaps is therefore consistent with the one deduced above from kinetics studies. The plots for barium and calcium

soaps of XSO are not shown in Figure 2. However, their values lie between those of Pb-XSO and Cd-XSO (Table 3).

Figure 3 is the i.r. spectrum for degraded PVC. There is absorption in the region 1580-1650cm^{-1}, which for degraded PVC, is normally associated with olefinic group. For PVC stabilized by metal soaps of XSO, two bands in the region 1500-1600cm^{-1} are apparent.
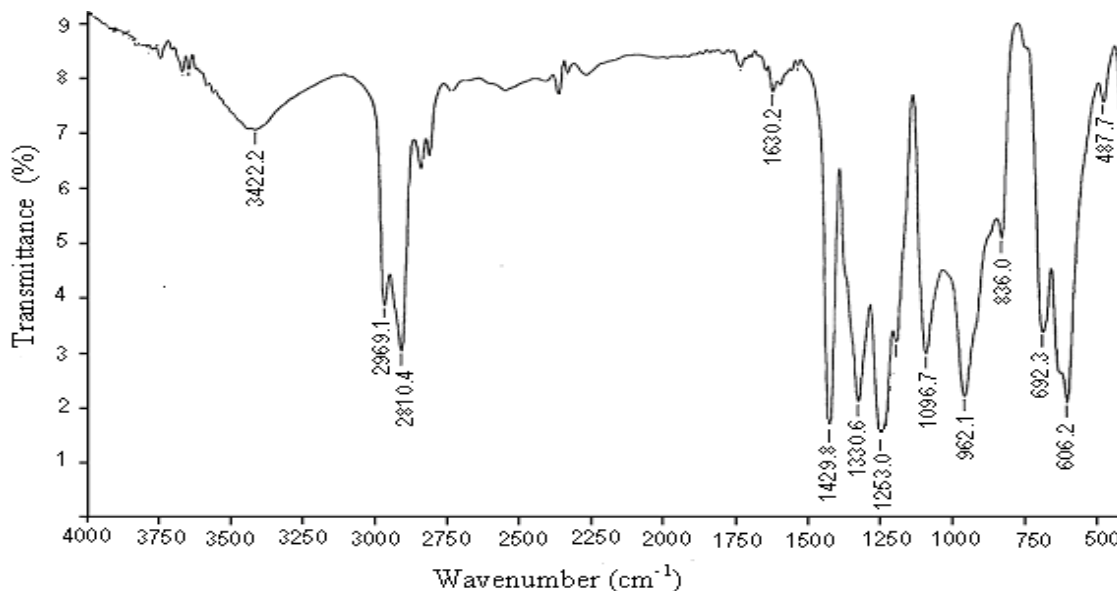

Figure 3: FT-IR Spectrum PVC film degraded at 160 ^{o}C without metal carboxylate

These bands are ascribed to symmetric and antisymmetric stretching vibrations of carboxylate group [15]. The summary of the absorption bands for PVC stabilized by all the metal carboxylates of XSO is represented in Table 4. The absorptions associated with carboxylate group vary within a narrow band for the soaps i.e., 1576-1577cm^{-1} and 1540-1541cm^{-1} for antisymmetric and symmetric vibrations respectively. This is to be expected given that the aggregate chemical characteristics of fatty acid constituents of the metal carboxylates are the same. Furthermore, the presence of the two bands suggests interaction of the carboxylates with PVC. The characteristic absorption of carbonyl group of an ester bonded to a polymer chain is observed in the region 1723-1728cm^{-1} for the metal carboxylates, and is consistent with Frye and Horst mechanism for exchange reaction of the allylic bonded chlorine atom of PVC by the ester group of metal carboxylates [15].

Table 4. FT-IR Bands for Interaction of PVC with Metal Carboxylates of XSO

PVC (alone)	Zn-XSO	Cd-XSO	Ba-XSO	Ca-XSO	Assignment of Band
3422	3404	3418	3400	3409	OH stretch
-	1723m	1728m	1727m	1724s	C = O stretch
1630w	-	-	-	-	C =C stretch
-	1541m	1540m	1541m	1540s	COO$^-$ sym. stretch
	1577m	1577m	1577m	1576s	COO$^-$ asym. stretch
692s	694s	694s	692s	694s	C –Cl stretch

m, medium; s, strong; w, weak.

The TG analysis was carried out to further establish the stabilizing effects of individual carboxylates on thermal degradation of PVC and to determine the synergistic effects of mixtures of the carboxylates on thermal stabilization of PVC. The thermogram of PVC samples containing the metal carboxylates is shown

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in Figure 4. The temperatures at which maximum degradation, t_{max} and various extents of degradation occurred were used to evaluate the stabilizing effects of the additives. The results of the analysis are presented in Table 5. From the result, the order of stabilization based on t_{max} is Pb-XSO>Ba-XSO>Ca-XSO>Cd-XSO>Zn-XSO. Indeed, for Zn-XSO, there is no stabilization since the t_{max} of 255.6 ^{o}C is less than the value, 298.0 ^{o}C, for PVC without additive. It is note-worthy that the two carboxylates of XSO with Lewis acidity property, Zn-XSO and Cd-XSO, exerted the least stabilizing effect on PVC, thus, the high level of unsaturation in the oil is antithetical to Lewis acidity (Figure 4).

Table 5. Evaluation of relative thermal stability of PVC stabilized with metal carboxylates of XSO

Additive	Temperatures at which various extents of degradation were attained				
3 % (w/w)	t_{max} (^{o}C)	5%	10%	30%	50%
None	298.0	234.9	275.9	308.6	330.0
Zn-XSO	255.6	256.5	264.2	301.1	334.0
Cd-XSO	315.5	263.1	300.7	324.9	344.7
Pb-XSO	322.0	286.4	307.7	332.2	353.6
Ba-XSO	321.5	273.8	304.8	332.6	354.2
Ca-XSO	320.1	282.0	302.1	330.8	353.1

Combination of alkaline earth carboxylates with covalent metal carboxylates exhibits synergistic effect in PVC thermal stabilization. This mixed metal carboxylates are usually in form of Ca/Zn and Ba/Cd carboxylates. The synergism is attributed to fast exchange reactions between the chlorides of Zn or Cd and carboxylates of Ca and Ba [16]. Synergistic effects of Ca/Zn and Ba/Cd mixed carboxylates of the metal carboxylates of the oil were investigated using different compositions and the result presented in Table 6. For the binary mixtures of Ca/Zn soaps, 90 wt%Ca/Zn mixture exhibited synergistic effect with the highest t_{max} value of 324.0 ^{o}C. For the mixture of Ba/Cd soaps, 90 wt% Ba/Cd mixtures also exhibited synergistic effect with the highest t_{max} value of 324.1 ^{o}C. These two t_{max} values are higher than those for individual metal carboxylates and that formed the basis for the synergistic effect. Other compositions have t_{max} values in the range of that of individual carboxylates which indicates that the effect of the mixture at these compositions is additive.

Table 6. Evaluation of relative thermal stability of PVC stabilized (3 %w/w) with binary mixtures of metal carboxylates of XSO

Ca-XSO/	Temperatures at which various extents of degradation were attained				
Zn-XSO	t_{max} (^{o}C)	5%	10%	30%	50%
90 wt%Ca-XSO	324.0	288.8	308.6	334.3	357.1
50 wt%Ca-XSO	256.5	259.9	271.3	307.7	336.6
10 wt%Ca-XSO	268.3	273.1	284.3	314.1	342.6
Ba-XSO/					
Cd-XSO					
90 wt%Ba-XSO	324.1	289.4	309.6	334.6	357.7
50 wt%Ba-XSO	321.9	286.3	308.1	332.0	354.7
10 wt%Ba-XSO	321.1	288.7	307.9	331.1	354.1

Epoxides are HCl scavengers and are effective in allylic chlorine atoms replacement in the polymer chain [5]. Many workers have reported on the enhancement of stabilizing effect of metal carboxylates in the presence of epoxidized oils [5, 15, 17]. The effect of the native and epoxidized oils on the zinc soap of the oil was investigated and the result presented in Table 7. The compositions of the mixture investigated were 10 wt% and 20 wt% oil/zinc soap. The results show that the native oil was more effective than the epoxidized in

enhancing the stabilizing effect of zinc soap based on t_{max} and temperatures at which various extents of degradation were attained. Specifically, t_{max} for 20 wt% XSO/Zn-XSO mixture is 295.2 °C as against a value of 286.5 °C for 20 wt% EXSO/Zn-XSO mixture. This suggests that the native oil reacts more effectively with $ZnCl_2$ than the epoxidized derivative. This could be explained based on high level of unsaturation in the native oil. The multiple bonds in the oil could act as $ZnCl_2$ trap in a manner similar to that for HCl [12] thereby making it less available for its autocatalytic effect on PVC degradation.
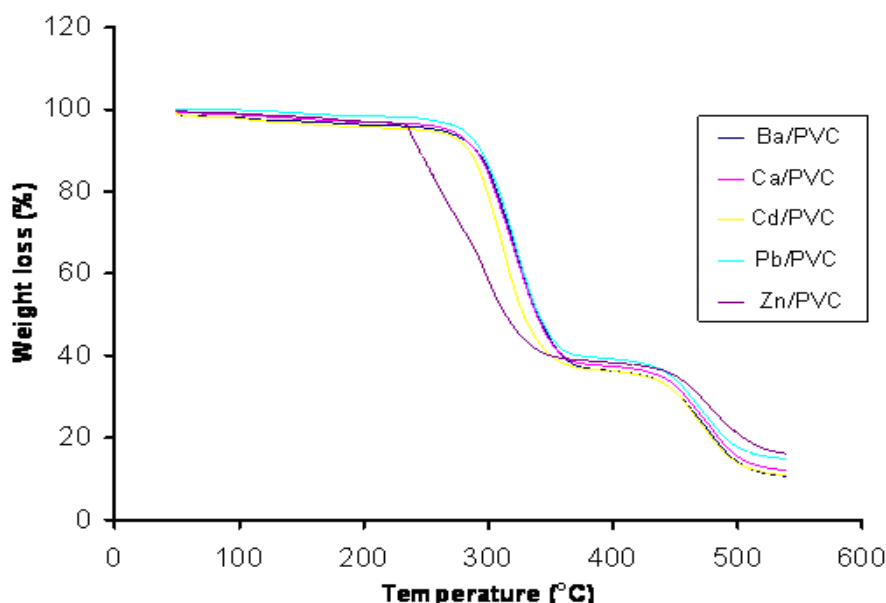

Figure 4: Thermogram of PVC samples containing the metal carboxylates

Table 7. Evaluation of relative thermal stability of PVC stabilized with mixtures of oil and Zn-XSO

Additive	Temperatures at which various extents of degradation were attained				
3 % (w/w)	t_{max} (°C)	5%	10%	30%	50%
10 wt% XSO	243.5	246.7	258.8	291.7	321.9
10 wt% EXSO	243.5	246.0	257.8	289.7	320.4
20 wt% XSO	295.2	265.8	279.6	305.5	331.5
20 wt% EXSO	286.5	256.3	270.2	298.7	326.1

Conclusion

PVC was stabilized by lead, barium, calcium and cadmium carboxylates of XSO under nitrogen atmosphere in the temperature range, 170-190°C. The order of stabilization was, Pb-XSO>Ba-XSO>Ca-XSO>Cd-XSO, corroborated by results of intrinsic viscosity measurements of degraded PVC samples and thermogravimetric analysis. The relative intrinsic viscosity of degraded PVC decreased linearly with increase in degradation time and suggested absence of secondary reactions of polyene. The mechanism of stabilization of PVC by the metal carboxylates is composite, consisting of HCl trapping reactions and substitution of labile chlorine atoms by carboxylate groups. The latter was supported by infra-red spectroscopy by the appearance of bands in the regions, 1576-1577cm^{-1} and 1540-1541cm,$^{-1}$ characteristic of carboxylate group antisymmetric and symmetric absorptions respectively. The calculated activation energies for PVC degradation in the presence of the carboxylates were consistent with the order of stabilization, having a value of 85.3 kJmol^{-1} for PVC/Ba-XSO composition. Mixed metal carboxylates of Ca/Zn and Ba/Cd exerted synergistic effect on PVC stabilization at the ratio of 9:1. Zn-XSO accentuated the degradation of PVC at a rate 5-fold higher than

the value in the absence of additive at 190°C, however, the oil (native and epoxidized) reduced the catastrophic effect of Zn-XSO on PVC degradation with the native oil exhibiting higher effectiveness.

Acknowledgements

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