



## Thermal Stability Study of some Metal Carboxylates of Castor (*Ricinus communis*) Seed oil on Poly(vinyl chloride)

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### Abstract

Barium, calcium, magnesium and zinc carboxylates of castor seed oil (CSO) were prepared by metathesis in aqueous ethanol. The FTIR spectra of the carboxylates showed two asymmetric vibrations and two symmetric vibrations of the carboxylate group. The two asymmetric vibrations occurred in the range 1573 - 1535  $\text{cm}^{-1}$  while the two symmetric vibrations were observed in the range 1491 - 1409  $\text{cm}^{-1}$  indicating the binding mode of the carboxylate groups to the metal ion and confirmed their formation. PVC thermal stability investigation was carried out by static stability test at 160 and 180°C, and thermogravimetric analysis. The results revealed that the oil, the metal carboxylates and their mixtures stabilized PVC against thermal degradation. Based on static stability time,  $t_{ss}$  and temperature of onset of thermal degradation,  $T_{onset}$ , Ba-CSO was the most effective and the order of PVC stabilization by the metal carboxylates is Ba-CSO > Mg-CSO > Ca-CSO > Zn-CSO. The results also indicate that the mixed metal carboxylates are more effective than individual metal carboxylates.

**Keywords:** Thermal stabilization, Carboxylates, Poly(vinyl chloride), Metathesis, Seed oil.

### Introduction

Poly (vinyl chloride) is a versatile thermoplastic with varied applications in both flexible and rigid forms<sup>1</sup>. It is rarely used alone due to its morphology and thermal instability hence, its compounding and moulding involve different additives like plasticizers and stabilizers. When the percentage (w/w) of the added plasticizer is 15 – 40, it is often referred to as flexible PVC, however, if the amount is less, it is rigid PVC<sup>2</sup> and its processing requires the use of stabilizers. The stabilizers are often applied in weight percent of 3 – 5. If heat stabilizers had not been discovered, commercial importance of PVC would have remained elusive as a result of its degradation at higher temperatures<sup>3</sup>. The degradation is characterized by evolution of HCl from the polymer chain leading to formation of conjugated polyene system and subsequent discolouration with concomitant loss of physical and mechanical properties<sup>4</sup>. The addition of thermal stabilizers reduces colour formation, suppress evolution of HCl and inhibit autocatalytic degradation of PVC<sup>5</sup>. Mainly, the classes of thermal stabilizers in current use are lead salts, metal soaps (metal carboxylates) and organo-tin compounds. Based on environmental concern, metal soaps (metal carboxylates) and organo-tin compounds are safer than lead salts, and the latter are gradually being phased out.

Metal carboxylates could be prepared from pure fatty acids and triglycerides i.e. fat and oil. Carboxylates derived from seed oil are complex mixtures, arising from the complexity of the fatty acid profile of the oil, hence they are often poorly characterized.

That notwithstanding however, their use in hard-water applications and liquid hand soaps had increased due to their ability to provide desired high soap concentrations<sup>6</sup>. Sodium and calcium carboxylates, especially those having hydroxyl group in the fatty acid chain, are useful in skin and food products because of their surface-active nature. Carboxylates of barium, cadmium, lead, zinc and calcium have found application as thermal stabilizers of poly(vinyl chloride)<sup>7,8</sup>.

Our earlier reports<sup>3, 9-12</sup> showed that metal carboxylates of some seed oils could stabilize PVC as a result of being thermally stable within the temperature range employed for processing it.

Reports available in the literature showed that castor plant seed is an essential oilseed (40 – 60% oil)<sup>13</sup> and the oil contains a high proportion (80 - 90 % ) of ricinoleic (12-hydroxy-oleic) acid<sup>14</sup> which can serve as a feedstock for the preparation of many useful chemicals. It finds usefulness as a base for many cosmetics and a potential source of biodiesel. Our earlier report<sup>13</sup> showed preparation of copper and nickel carboxylates and their calcinated derivatives from castor seed oil that exhibited antimicrobial activity. Castor plant grows wildly in south western part of Nigeria and is rarely exploited and explored for any industrial application. There has not been any report on the utilization of the oil for preparation of barium, calcium, magnesium and zinc carboxylates and their evaluation as PVC thermal stabilizers. Therefore, what we aim at in this work is to prepare these carboxylates and evaluate their PVC thermal stability effect thereby adding value to the oil.

## Materials and Method

**Purification of poly(vinyl chloride):** Poly(vinyl chloride) sample was purified by soxhlet extraction with methanol for 5 hr followed by washing with hot water. The purified polymer was filtered off and dried at 50°C for 24 hr<sup>15</sup>.

**Preparation of metal carboxylates:** The castor oilseeds collected at Abeokuta, Ogun State were extracted with n-hexane using soxhlet extraction method. The carboxylates were prepared as earlier reported<sup>13</sup>. The salts used in the preparation of the carboxylates are analytical grade.

**FTIR spectroscopy of the carboxylates:** The FTIR spectra of the carboxylates were measured using a Thermo Scientific iS5 FTIR equipped with IR microscopy accessory and a germanium crystal at a resolution of 4cm<sup>-1</sup> between wave numbers 4000-400 cm<sup>-1</sup>.

**Thermal stability studies:** Static stability test (Congo red testing): This was carried out according to ASTM D4202<sup>4</sup>. Typically, 1.94 g of PVC and 0.06g of stabilizer were mixed in a mortar. The mixture was then put into a tube with Congo red test paper located at about 2 cm above the sample. The tube was heated with an oil bath at 160°C and 180°C for evaluating static thermal stability of PVC. The time when Congo red test paper began to turn blue was defined as static stability time (t<sub>ss</sub>)<sup>16</sup>.

**Thermogravimetric analysis (TGA):** Thermogravimetric study of PVC degradation in the presence of the metal carboxylates was conducted using Perkin-Elmer Pyris 6 thermal gravimetric analyser programmed at a heating rate of 20°C min<sup>-1</sup> up to a temperature of 550°C under nitrogen.

## Results and Discussion

The FTIR spectrum of the Zn carboxylate is presented in Figure-1, representing the spectra of other carboxylates due to the fact that they are similar. It revealed the binding mode of the carboxylate groups to the metal ions. All the metal carboxylates prepared are divalent and have two carboxylic acid moieties per molecule. As shown in the figure, the carboxylates have characteristic two asymmetric and two symmetric carboxylate vibrations indicating that they existed as bridging bidentate structures. For the zinc carboxylate, the two asymmetric vibrations occurred at 1572 cm<sup>-1</sup> and 1535 cm<sup>-1</sup> while the two symmetric vibrations were observed at 1491 cm<sup>-1</sup> and 1412 cm<sup>-1</sup>. The asymmetric vibrations of the carboxylate group of calcium carboxylate were observed at 1573 cm<sup>-1</sup> and 1532 cm<sup>-1</sup> and the two symmetric vibrations occurred at 1452 cm<sup>-1</sup> and 1401 cm<sup>-1</sup>. For magnesium and barium carboxylates, the asymmetric vibrations of the carboxylate group were observed at 1561 cm<sup>-1</sup> and 1560 cm<sup>-1</sup> respectively with symmetric vibrations occurring at 1447 – 1412 cm<sup>-1</sup> and 1429 – 1409 cm<sup>-1</sup> respectively. This is consistent with earlier reports on some carboxylates<sup>13,17,18</sup> thereby confirming their formation. The CH<sub>2</sub>

asymmetric and symmetric stretching vibrations of the alkyl group of the fatty acids occurred in the range 2918 - 2849 cm<sup>-1</sup> while the band at 3359 cm<sup>-1</sup> may be associated with hydrogen bonded OH groups, either from water or fatty acid portion of the carboxylate. Other carboxylates have similar characteristic IR bands. The fact that castor seed oil contains 80 – 90% ricinoleic acid indicates that its metal carboxylates are substantially ricinoleates.

The results of thermal stability studies revealed that all the four metal carboxylates of CSO, the seed oil and mixtures of the carboxylates stabilized PVC against thermal degradation (Figures-2, 3, 4 and 5). Static stability time, t<sub>ss</sub>, of PVC degradation carried out at 160 °C are as follows: PVC alone (8 min); PVC + 3 wt% oil (17 min); PVC + 6 wt% oil (23 min); PVC + 3 wt% Ba-CSO (23 min); PVC + 3 wt% Ca-CSO (16 min); PVC + 3 wt% Mg-CSO (22 min); PVC + 3 wt% Zn-CSO (13 min) (Figure-2). For the PVC degradation carried out at 180 °C, the result followed the same trend: PVC alone (3 min); PVC + 3 wt% oil (7 min); PVC + 6 wt% oil (15 min); PVC + 3 wt% Ba-CSO (10 min); PVC + 3 wt% Ca-CSO (7 min); PVC + 3 wt% Mg-CSO (9 min); PVC + 3 wt% Zn-CSO (5 min) (Figure-3). The results showed the effect of temperature on degradation of poly(vinyl chloride), t<sub>ss</sub> decreased with increase in temperature. Based on t<sub>ss</sub>, order of stabilization of PVC by metal carboxylates of CSO is Ba-CSO > Mg-CSO > Ca-CSO > Zn-CSO.

Various mixtures of mixed metal carboxylates were investigated at 180°C but those found to exhibit synergistic effect at 1 : 4 ratio are: PVC + 3 wt% Zn/Ba-CSO (13 min); PVC + 3 wt% Zn/Ca-CSO (17 min); PVC + 3 wt% Zn/Mg-CSO (16 min); PVC + 3 wt% Ba/Ca-CSO. (18 min); PVC + 3 wt% Ba/Mg-CSO (11 min); PVC + 3 wt% Ca/Mg-CSO (14 min) (Figure 4). The order of stabilization based on t<sub>ss</sub>, is Ba/Ca-CSO > Zn/Ca-CSO > Zn/Mg-CSO > Ca/Mg-CSO > Zn/Ba-CSO > Ba/Mg-CSO.

Figure-2 shows the influence of metal carboxylates of CSO and the oil on static stability time, t<sub>ss</sub>, of PVC at 160°C. It is apparent that PVC samples with incorporation of the additives have higher t<sub>ss</sub> values than PVC alone. PVC alone has t<sub>ss</sub> value of 8 min while those samples with additives have values in the range of 13 to 23 min. The sample incorporating Ba-CSO has the highest value of 23 min while the one incorporating Zn-CSO has the least value of 13 min. Those with incorporation of Ca-CSO and Mg-CSO have t<sub>ss</sub> values of 16 min and 22 min respectively. PVC samples that incorporated the oil have t<sub>ss</sub> values comparable to those that incorporated metal carboxylates. The sample that incorporated 3 wt% of oil has a value of 17 min while the one that incorporated 6 wt% of oil has a value of 23 min. The oil stabilized PVC and the effect increased with concentration. The stabilizing effect of oil has been attributed to trapping of HCl by addition reactions of the latter with unsaturated fatty acid moieties of the oil<sup>3</sup>. The high viscosity of the oil might have also contributed to the observed

effect as this could slow down splitting-off of HCl from the polymer backbone.

The results of static stability test carried out at 180°C are presented in Figure 3. The results are similar to those obtained when the test was carried out at 160 °C albeit with lower  $t_{ss}$  values. PVC sample without additive has  $t_{ss}$  value of 3 min while those with incorporation of additives have  $t_{ss}$  value in the range 5 – 16 min. of the PVC samples, sample that incorporated Ba-CSO has the highest value of 10 min while sample that incorporated Zn-CSO has the least value of 5 min. Those with incorporation of Ca-CSO and Mg-CSO have  $t_{ss}$  values of 7 min and 9 min respectively. PVC sample that incorporated 3 wt% of oil has a value of 7 min while the one that incorporated 6 wt% of oil has a value of 15 min. This result lends credence to the possible effect of viscosity of the oil on its ability to stabilize PVC at these temperatures. On the basis of  $t_{ss}$ , order of stabilization of PVC by the carboxylates is Ba-CSO > Mg-CSO > Ca-CSO > Zn-CSO. This is consistent with earlier reports on the ability of metal carboxylates to stabilize PVC against thermal degradation<sup>3,7,8,12,19,20</sup>.

Effective PVC thermal stabilizers are usually mixtures of similar or different chemical compounds<sup>4,5,16</sup>, this is due to the ability of the mixtures to exhibit synergism. Reports available in the literature revealed that mixtures of metal carboxylates exhibit this effect<sup>12,21</sup>. Synergism had been ascribed to fast exchange reactions between the chlorides of metals with Lewis acid character (e.g. Zn, Cd) and carboxylates of alkaline-earth metals (e.g. Ca, Ba). Synergistic effects of mixtures of the carboxylates were investigated at 180°C using varied compositions but some of the mixtures in the ratio 1: 4 were effective and the result is presented in Figure-4. PVC samples containing these mixed carboxylates exhibited  $t_{ss}$  values higher than the samples containing individual metal carboxylates. The value range from 11 min for sample containing Ba/Mg-CSO to 18 min for sample that incorporated Ba/Ca-CSO. The order of stabilization based on  $t_{ss}$ , is Ba/Ca-CSO (18 min) > Zn/Ca-CSO

(17 min) > Zn/Mg-CSO (16 min) > Ca/Mg-CSO (14 min) > Zn/Ba-CSO (13 min) > Ba/Mg-CSO (11 min). Although synergism is ascribed to fast exchange reactions between the chlorides of metals with Lewis acid character and carboxylates of alkaline-earth metals, each of these carboxylates has capacity to absorb evolved HCl in addition to substitution of labile chlorine atoms<sup>15</sup>. This might have contributed to their effectiveness.

To further evaluate the efficacy of individual carboxylates as PVC heat stabilizer, TG. analysis was carried out and the thermogram is presented in Figure 5. The temperatures of onset of thermal degradation,  $T_{onset}$  and at which different extents of degradation occurred were used to evaluate the stabilizing effects of the additives. These are presented in Table 1. Based on the result, all the carboxylates stabilized PVC against thermal degradation with Ba-CSO being the most effective. This result is consistent with the results of static stability test.

## Conclusion

The suitability of castor seed oil in preparing environment-friendly PVC thermal stabilizers was investigated. The extracted oilseed gave an oil yield of 51.3 % (w/w). Four metal carboxylates were prepared via metathesis in aqueous ethanol. The formation of the carboxylates was confirmed by FTIR spectrophotometry. Thermal stabilizing effects of the oil and the carboxylates on PVC were investigated by static stability test and thermogravimetric analysis.

The oil, the metal carboxylates and their mixtures stabilized PVC against thermal degradation, however, the mixtures at 1 : 4 ratio exhibited synergism and are effective than individual carboxylates within the experimental conditions. The results suggest that CSO could serve as a source of environment-friendly PVC thermal stabilizers.

**Table-1**  
**Evaluation of relative thermal stability of PVC stabilized with metal carboxylates of CSO**

Additive (3wt%)	Temperatures at which different extents of degradation were attained (°C)				
	$T_{onset}$	5%	10%	30%	50%
None	210	216	252	283	306
Ba-CSO	258	263	289	323	339
Ca-CSO	224	233	271	285	307
Mg-CSO	240	245	280	315	327
Zn-CSO	222	230	272	286	307

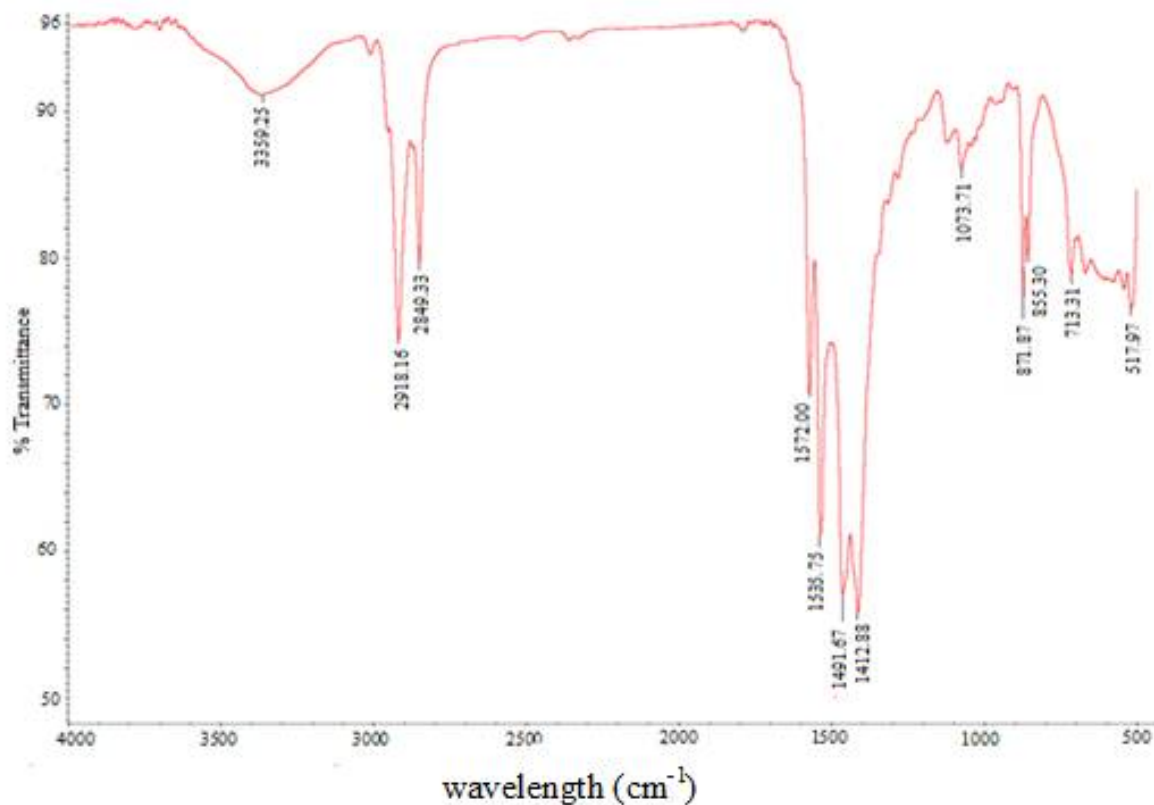


Figure-1  
FTIR spectrum of Zn carboxylate

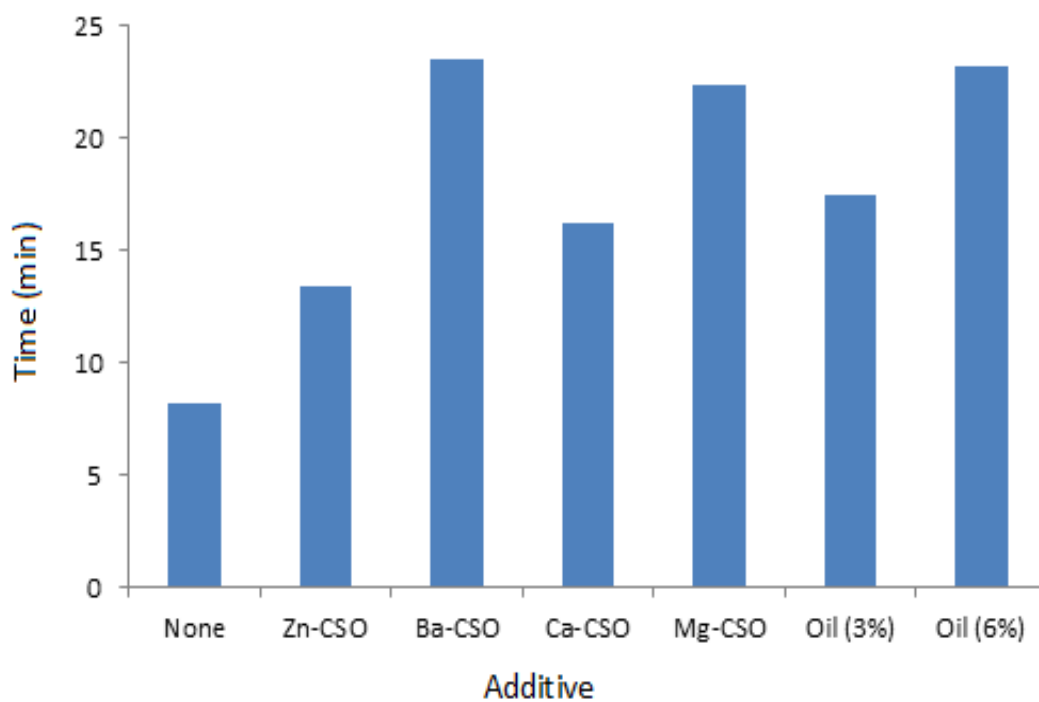


Figure-2  
Effect of 3 wt% metal carboxylates of CSO on PVC at 160°C

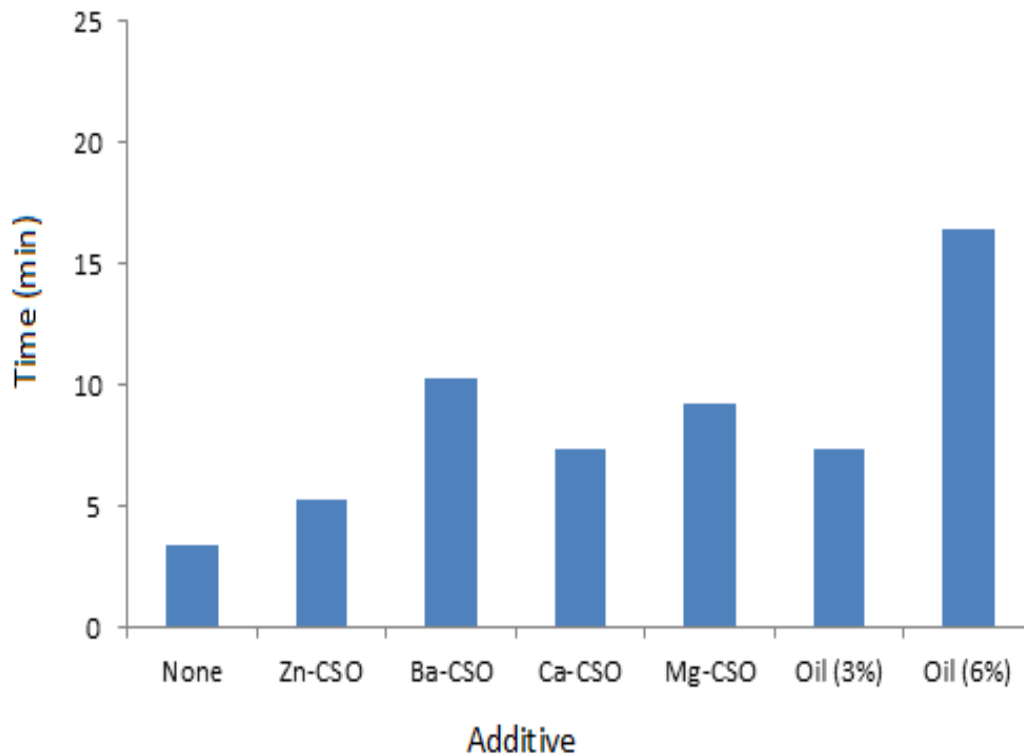


Figure-3  
Effect of 3 wt% metal carboxylates of CSO on PVC at 180°C

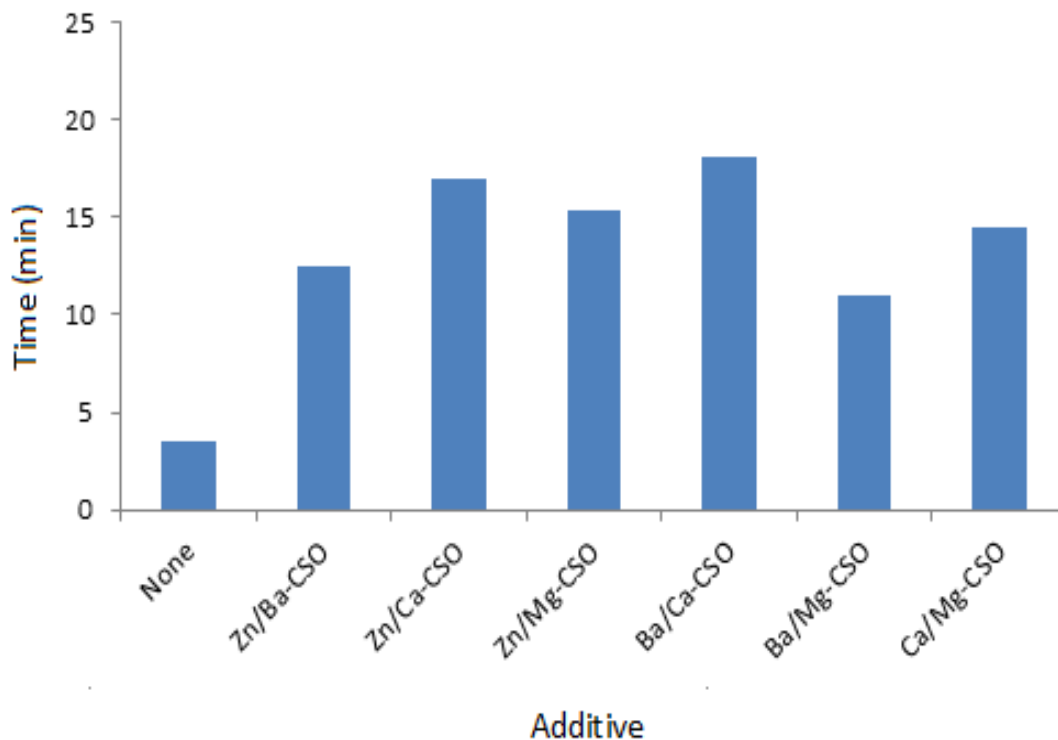
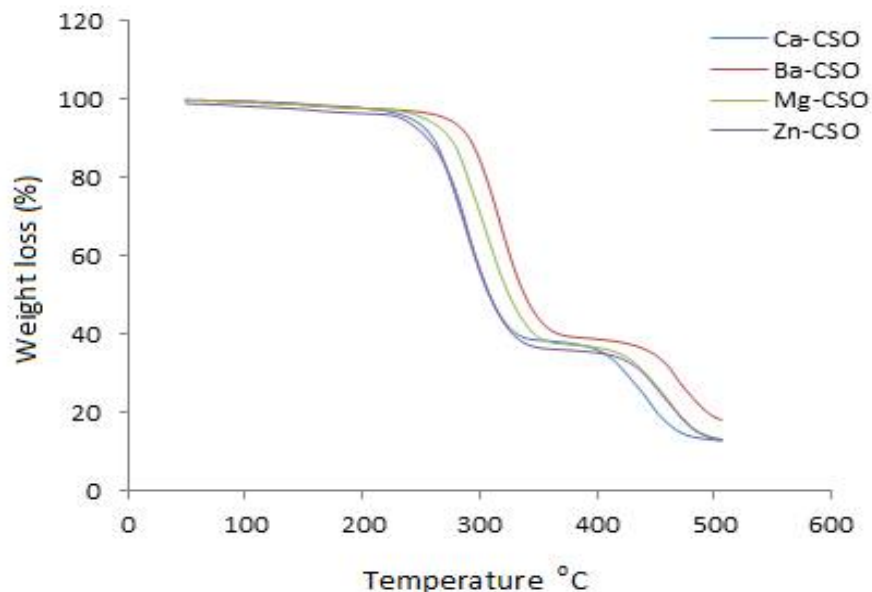


Figure-4  
Effect of 3 wt% mixed metal carboxylates of CSO on PVC at 180°C



**Figure-5**  
**Thermogram of PVC containing 3 wt% of metal carboxylates of CSO**

## References

1. Folarin O.M. and Sadiku E.R. (2011). Thermal stabilizers for poly(vinyl chloride): A review. *Int. J. Phys. Sci.*, 6(18), 4323-4330.
2. Yoshioka T., Kameda t., Leshige M. and Okuwaki A. (2008). Dechlorination behaviour of flexible poly(vinyl chloride) in NaOH/EG solution. *Polym. Degrad. Stab.*, 93(10), 1822-1825.
3. Folarin O.M., Eromosele I.C. and Eromosele C.O. (2012). Thermal Stabilization of Poly(vinyl chloride) by Metal Carboxylates of Ximenia americana Seed Oil Under Inert Condition. *J. Mat. Environ. Sci.*, 3(3), 507-514.
4. Mohamed N.A. and Al-mehbad N.Y. (2009). Thermal degradation behaviour of poly(vinyl chloride) in the presence of poly(*N'*-acryloyl benzhydrazide). *Polym. Degrad. Stab.*, 94(4), 540-543.
5. van Es D.S., Steenwijk J., Frissen G.E., van der Kolk H.C., van Haveren J., Geus J.W. and Jenneskens L.W. (2008). The compatibility of (natural) polyols with heavy metal- and zinc-free poly(vinyl chloride): Their effect on rheology and implications for plate-out. *Polym. Degrad. Stab.*, 93(1), 50-58.
6. Myers D. (2006). *Surfactant Science and Technology*. 3<sup>rd</sup> Ed. John Wiley and Sons, Inc., Hoboken, New Jersey. 64.
7. Bacaloglu R. and Fisch M. (1994). Degradation and stabilization of poly(vinyl chloride). I. Kinetics of the thermal degradation of poly(vinyl chloride). *Polym. Degrad. Stab.*, 45(3), 301-313.
8. Owen E.D. and Msayib K.J. (1989), Catalyzed degradation of poly(vinylchloride). III. Zinc(II) chloride catalysis. *J. Polym. Sci.*, 27(2), 399-408.
9. Folarin O.M. and Enikanoselu O.N. (2010). *EJEAF Che.*, 9,1604-1610.
10. Folarin O.M., Siyanbola T.O. and Shittu A.T. (2011). *EJEAF Che.*, 10, 2623-2628.
11. Folarin O.M., Eromosele I.C. and Eromosele C.O. (2011). *Sci. Res. Essays.*, 6, 1922-1927.
12. Folarin O.M., Eromosele I.C. and Eromosele C.O. (2013). *Environ. Nat. Res. Research.*, 3, 1-9.
13. Folarin O.M., Olumayede E.G., Nwachukwu P.C. and Fakoya S. (2013). *J. Appl. Sci. Environ. Manage.*, 17, 483-490.
14. Salager J. (2002). *Surfactants: Types and Uses*. FIRP booklet # E300-A. Universidad de los Andes Venezuela, 40.
15. Wypych G. (2008). *PVC Degradation and stabilization*. 2<sup>nd</sup> Ed. Chem Tec Publishing, Toronto, Canada. 295.
16. Fang L., Song Y., Zhu X. and Zheng Q. (2009). *Polym. Degrad. Stab.*, 94, 845-850.
17. Roy P.K., Surekha P., Rajagopal C. and Choudhary V. (2006). *Polym. Degrad. Stab.*, 91, 1980-1988.
18. Jona E., Ondrusova D., Pajtasova M., Simon P. and Michaler J. (2001). *J. Appl. Polym. Sci.*, 81, 2936-2943.
19. Egbuchunam T.O., Balkose D. and Okieimen F.E. (2007). *Polym. Degrad. Stab.*, 92, 1572-1582.
20. Okieimen F.E. and Eromosele C.O. (2000). *Eur. Polym. J.*, 36, 525-537.
21. Balkose D., Gokcel H.I. and Goktepe S.E. (2001). *Eur. Polym. J.*, 37, 1191-1198.