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Thermal degradation of poly(vinyl chloride) in the presence of *Ximenia americana* and *Balanites aegyptiaca* seed oils

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Ximenia americana **seed oil (XSO) and** *Balanites aegyptiaca* **seed oil (BSO) were soxhlet extracted and characterized. The iodine values were 158.3 and 102.6 gI$_2$ 100 g^{-1} for XSO and BSO, respectively. The oxirane content for the epoxidized oil derivatives, EXSO and EBSO, were 4.9 and 4.1%, respectively. Kinetic studies of thermal degradation of poly (vinyl chloride), (PVC) in the temperature range, 170 to 190°C under nitrogen atmosphere were conducted in the presence of the oils and epoxidized derivatives. The effect of the oils was evaluated from the rate of dehydrochlorination at 1% degradation, R$_{DH}$ and the time required for degradation to attain 1% conversion t$_{DH}$. The additives retarded dehydrochlorination rate of PVC. The mechanism of thermal stabilization of PVC by the oils was attributed to trapping of HCl through addition reactions of the latter with unsaturated fatty acids. The resultant order of stabilization was, EXSO > EBSO > XSO > BSO. The latter was consistent with the results of viscosity measurements on degraded polymer and from thermogravimetric studies. The order of stabilization was corroborated by the activation energies, (E$_a$) calculated from the rate constants of dehydrochlorination process. The highest value of 111.84 kJmol^{-1} was obtained for PVC with 3 wt-% EXSO additive. In air, PVC was unstabilized by XSO and BSO and was adduced to dominant oxidative reactions of unsaturated fatty acids and consequent prevention of HCl-trapping addition reactions.**

Key words: Thermal degradation, stabilization, poly(vinyl chloride), *Ximenia americana, Balanites aegyptiaca,* seed oils.

INTRODUCTION

Poly(vinyl chloride) is a commodity plastic that is widely used in both flexible and rigid forms as water pipes, floor and roof tiles, packaging films and sheets due to its non-flammable nature, good performance and low cost (Yoshioka et al., 2008; Tong et al., 2011). It is less stable than many other plastomers and undergoes degradation by the impact of heat, oxygen, light and mechanical energy (Vrandecic et al., 2004). At elevated temperature, it degrades via thermal dehydrochlorination that is auto-accelerated by the released HCl which results in severe discolouration due to the formation of conjugated double bonds in the polymer chain and consequent loss of some

properties (Tong et al., 2011; Toliwal and Patel, 2009; Liu et al., 2008; Steenwijk et al., 2006). HCl is believed to sustain the auto-catalytic process (Levchik and Weil, 2005) and stabilizers that can irreversibly bond HCl prevent or delay the degradation process. Thus, a number of stabilizers have been used in processing of PVC. These include metal salts of organic acids, organometallic compounds, inhibitors of radical chain reactions and polyols (Liu et al., 2008; van Es et al., 2008; Steenwijk et al., 2006; Levchik and Wen, 2005; Sabaa et al., 2003; Mohamed et al., 2000). The mechanism of stabilization of PVC by the stabilizers involves substi-tution of labile chlorine atoms in the polymer and consequent inhibition or retardation of hydrogen chloride elimination reaction (Bensemra et al., 1989); scavenging of hydrogen chloride or reversibly blocking of growth of polyene (Ivan et al., 1991), depending on the nature of

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stabilizer. Recent reports have shown that seed oils can stabilize PVC against thermal degradation but the mechanism of the process is not understood. However, there is evidence that the presence of unsaturation in the fatty acid moiety of oils reduces the stabilizing effect of metal soaps derivatives on PVC (Okieimen and Ebhoaye, 1993). The present study is on the use of two seed oils, namely, *Ximenia americana* (wild olive) and *Balanites aegyptiaca* (Betu) and their epoxidized derivatives for stabilization of PVC. *X. americana* plant is a shrub of the family Olacaeae. It produces a small, yellow plum fruits which are edible with oily seed kernel. *B. aegyptiaca* plant is a small-sized tree of the family Zygophyllaceae. Its ripe fruits are edible with oily seed kernel (Keay, 1989). In this article, the features of the thermal and thermo-oxidative degradation of PVC in the presence of the oils and their epoxidized derivatives are reported and discussed.

MATERIALS AND METHODS

Poly(vinyl chloride), obtained from Sigma-Aldrich Co (USA) (Mn, 0.9 × 10^5) was purified by dissolution in cyclohexanone and precipitated with constant stirring in excess methanol. The precipitated polymer was filtered off after 24 h, washed with methanol and air-dried at 50°C. *X. americana* seed oil (XSO) and *B. aegyptiaca* seed oil (BSO) were soxhlet – extracted with petroleum ether (40 to 60°C) from their seeds obtained from Yola, Adamawa state, Nigeria and characterized by standard methods (Hamilton, 1992).

Epoxidation of seed oils

Epoxidation of XSO and BSO was carried out using literature methods (Gan et al., 1992; Frederick, 1970). The extent of epoxidation of the oils, calculated as percentage oxirane were 4.9 and 4.1% for XSO and BSO, respectively.

Fatty acid composition of oils

The fatty acid composition, of XSO and BSO were determined from the methyl ester derivatives by gas chromatography – mass spectrometry (GC – MS) using Agilent 6890 – 5973N GC – MSD equipped with DB–5MS column (60 m × 0.25 mm × 0.15 μm). Carrier gas was helium at constant flow rate of 1 ml min^{-1}. The injector temperature was 250°C; column temperature was raised to 220°C at a heating rate of 10°C min^{-1}.

Degradation of PVC

Thermal degradation of PVC was conducted in the presence of XSO, BSO and their epoxidized derivatives in the temperature range, 170 to 190°C in air and under nitrogen atmosphere. Typically, PVC sample (1 g) which was mixed thoroughly with a known amount of the oil or derivative was put in a degradation tube fitted to a source of dry nitrogen gas at flow rate of 60 ml min^{-1}. The degradation tube was immersed in a thermo-stated oil bath at an appropriate temperature controlled to within ±1.0°C. The HCl evolved at regular intervals of time was passed into a standard sodium hydroxide solution. The latter was back-titrated with standard hydrochloric acid to determine the extent of dehydro-chlorination (Eromosele, 1998).

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±0.2°C. The intrinsic viscosity [η] was determined from the Huggins equation:

$$\eta_{sp}/C = [\eta] + K^1 [\eta]^2 C.$$

The stabilizing effects of the oils and derivatives were evaluated from the ratios of the intrinsic viscosity of PVC samples degraded in the presence of additives to the viscosity of undegraded sample, that is, $[\eta]/[\eta]_0$.

Thermogravimetric study of PVC degradation

Thermogravimetric study of PVC degradation in the presence of XSO, BSO and derivatives were carried out using Perkin-Elmer Pyris 6 thermal gravimetric analyzer programmed at a heating rate of 10°C min^{-1} up to a temperature of 550°C under nitrogen.

RESULTS

The physico-chemical characteristics and fatty acid composition of XSO and BSO are shown in Table 1. Kinetics of degradation of PVC in the presence XSO and BSO under nitrogen are presented in Table 2 while Table 3 shows intrinsic viscosities of degraded PVC is air in the presence of the oils at 190°C. The kinetics of thermal dehyrochlorination of PVC in the presence of EXSO and EBSO under nitrogen are presented in Table 4 and the intrinsic viscosities of degraded PVC under nitrogen in the presence of the oils and epoxidized derivatives at 190°C are presented in Table 5. Table 6 shows the activation energies of the degradation of PVC in the presence of the oils and their epoxidized derivatives under nitrogen while thermal stabilities of the oils, their epoxidized derivatives and PVC in the presence of the oils and derivatives under nitrogen are presented in Table 7. The degradation of PVC without additive under nitrogen atmosphere and in the temperature range, 170 to 190°C is represented in Figure 1. Figure 2 represents the plots for the degradation of PVC in the presence of EXSO under nitrogen while Figure 3 shows the plot of relative viscosity $[\eta]/[\eta]_0$ versus degradation time for PVC degraded under nitrogen in the presence of XSO and BSO at 170°C. Thermal stabilities of the oils and their epoxidized derivatives are presented in Figures 4 and 5.

DISCUSSION

The dominant fatty acids in the oils are oleic and linoleic acids which constitute 83.25 and 86.01% of the acids for

Table 1. Physico-chemical characteristics and fatty acid profiles of XSO and BSO.

Characteristics	Values	
	XSO	**BSO**
Oil content (% w/w)	50.2	44.8
Specific gravity (30°C)	0.972	0.961
Refractive index (20°C)	1.472	1.468
Iodine value (gI_2/100 g)	158.30	102.6
Saponification value ($mgKOHg^{-1}$)	191.36	170.42
Peroxide value ($mEqkg^{-1}$)	15.42	13.14
Acid value ($mg\ KOHg^{-1}$)	0.16	10.26
Free fatty acid ($mg\ KOHg^{-1}$)	0.08	5.13
Fatty acid composition (wt %):		
Palmitic acid	2.74	8.0
Stearic acid	1.64	5.79
Oleic acid	66.72	34.52
Linoleic acid	16.53	51.49
Linolenic acid	0.38	-
Gadoleic acid	1.58	-
Stearolic acid (9-octadecynoic acid)	0.92	-
Unidentified	9.49	

Table 2. Kinetics of thermal dehydrochlorination of PVC in the presence of *Ximenia americana* and *Balanites aegyptiaca* seed oils.

Additive	Temperature (°C)	t_{DH}(min)	$10^2 R_{DH}$(%min^{-1})	Rate constant k_1 (min^{-1})
	170	78	1.76	1.10
None	180	56	1.90	1.19
	190	34	3.00	1.88
XSO 3 wt-%	180	80	1.50	0.94
	190	49	2.50	1.56
XSO 6 wt-%	180	82	1.45	0.91
	190	49	2.74	1.71
BSO 3 wt-%	180	58	1.72	1.08
	190	36	2.80	1.75
BSO 6 wt-%	180	75	1.67	1.04
	190	45	2.92	1.83
50/50(XSO/BSO)	180	73	1.80	1.13
3 wt-%	190	45	2.86	1.79

XSO and BSO, respectively. XSO has the distinctive feature of containing linolenic acid and stearolic acid (9-octadecynoic acid) with a triple bond. This feature may account for the marked difference in iodine values for the oils that is, 158.3 and 102.6 gI_2/ 100 g for XSO and BSO respectively. Thus, the iodine value for XSO is a factor of 1.5 higher than that of BSO. The oil content of 50.2% (w/w) for XSO confirms a previous report (Eromosele et al., 1998). The reasonably high amounts of unsaturated fatty acids coupled with the relatively high iodine values of the oils justify their selection for epoxidation. Oxirane numbers of the two epoxidized oils EXSO (4.9%) and

Table 3. Intrinsic viscosity for PVC degraded in air at 190°C in the presence of oils.

Additive	Degradation time (min)	$[\eta]$ (dl/g)	$[\eta]/[\eta]_o$
	30	1.22	0.78
	60	0.85	0.54
None	80	0.69	0.44
	100	0.57	0.37
	120	0.50	0.32
	30	1.22	0.78
	60	0.85	0.54
XSO 6 wt-%	80	0.68	0.43
	100	0.58	0.37
	120	0.51	0.33
	30	1.22	0.78
	60	0.84	0.54
BSO 6 wt-%	80	0.68	0.44
	100	0.57	0.37
	120	0.50	0.32

Table 4. Kinetics of thermal dehydrochlorination of PVC in the presence of epoxidized *Ximenia americana* and *Balanites aegyptiaca* seed oils under nitrogen.

Additive	Temperature(°C)	t_{DH} (min)	$10^2 R_{DH}$ (min^{-1})	Rate constant, k_1(%min^{-1})
EXSO 3 wt-%	180	87	1.43	0.89
	190	62	2.70	1.69
EBSO 3 wt-%	180	81	1.60	1.00
	190	47	2.86	1.79

EBSO (4.1%) indicate fair amount of epoxidation and introduction of epoxy group.

The rate of degradation, R_{DH} measured at 1% conversion, are 1.76×10^{-2}, 1.9×10^{-2} and 3.0×10^{-2}% min^{-1} at 170, 180 and 190°C respectively for PVC degraded without additive under nitrogen atmosphere (Figure 1). The corresponding times for degradation to attain 1% conversion, t_{DH} are 78, 56 and 34 min. There is an induction period of 15 min for degradation at 170°C. In the presence of 3 wt-% XSO and under nitrogen atmosphere, the conversion in dehydrochlorination of PVC over the same temperature range is similar. The induction period is 25 min at 170°C and is a factor of 1.5 higher than the corresponding value in the absence of XSO. The t_{DH} values are 80 and 49 min at 180 and 190°C, respectively. The corresponding rates of degradation are 1.5×10^{-2} and 2.5×10^{-2}% min^{-1}. At 170°C, the conversion at 120 min degradation time is less than 1%. Although the rates of degradation of PVC in the absence and presence of XSO are within the same order of magnitude, that is, 10^{-2}% min,$^{-1}$ there is significant increase in t_{DH} by up to 44% at 180 and 190°C

in the presence of XSO. Thus, XSO exerts stabilizing effect on PVC against thermal degradation under nitrogen conditions. Similar effect has been reported for jatropha seed oil at 10 wt-% concentration at 170 to 180°C. At 190°C however, jatropha seed oil did not stabilize PVC (Okieimen and Sogbaike, 1995). An increase in the weight concentration of XSO from 3 to 6% is not accompanied by a corresponding increase in the stabilizing effect of the oil on the degradation process (Table 2). In the presence of 3 wt-% BSO, PVC is not stabilized, having t_{DH} values which are within ±5% of the ones in the absence of the oil, as shown in Table 2. However, at 6 wt-% BSO, PVC is stabilized by the oil with t_{DH} values of 75 and 45 min at 180 and 190°C, respectively. The corresponding R_{DH} values are 1.67×10^{-2} and 2.92×10^{-2}% min^{-1}. Furthermore, it is characterized by an induction period of 20 min at 170°C.

It is to be noted that the t_{DH} values for 3 wt-% XSO are comparable to those of 6 wt-% BSO albeit the latter, at twice the concentration of the former. Thus, XSO exerts a higher stabilizing effect on PVC than BSO at equivalent concentrations under nitrogen conditions. The results for

Table 5. Intrinsic viscosity for PVC degraded under nitrogen at 190°C in the presence of oils and derivatives.

Additive	Time of degradation (min)	$[\eta]$ (dl/g)	$[\eta]/[\eta]_o$	(%) reduction in $[\eta]$
None	30	0.95	0.60	40
	60	0.52	0.33	
	80	0.37	0.24	
	100	0.28	0.18	
	120	0.18	0.12	88
XSO 6 wt-%	30	1.08	0.69	31
	60	0.68	0.43	
	80	0.45	0.28	
	100	0.33	0.21	
	120	0.27	0.17	83
EXSO 3 wt-%	30	1.10	0.70	30
	60	0.71	0.45	
	80	0.47	0.30	
	100	0.39	0.25	
	120	0.31	0.20	80
BSO 6 wt-%	30	1.05	0.67	33
	60	0.67	0.43	
	80	0.45	0.28	
	100	0.33	0.21	
	120	0.24	0.15	85
EBSO 3 wt-%	30	1.08	0.69	31
	60	0.69	0.44	
	80	0.47	0.30	
	100	0.36	0.23	
	120	0.28	0.18	82

$[\eta]_0 = 1.563 \pm 0.017$.

Table 6. Activation energies for thermal degradation of PVC under nitrogen in the presence of XSO, BSO and epoxidized derivatives.

| Additive	Activation Energy, kJmol^{-1}
None	79.76
XSO 3 wt-%	88.35
BSO 3 wt-%	84.18
EXSO 3 wt-%	111.84
EBSO 3 wt-%	101.54

dehydrochlorination of PVC in the presence of 50/50 blend of XSO/BSO at 3 wt-% under nitrogen in the temperature range, 170 to 190°C are shown in Table 2 and it is apparent that the stabilization of PVC by the oil blend is non-synergistic. From the results, the mechanism for stabilization of PVC by the oils may be adduced to trapping of HCl by addition reactions of the latter with unsaturated fatty acid moieties under nitrogen atmosphere. The resultant effect is a concomitant retardation of HCl-catalyzed degradation of the polymer. This mechanism is analogous to stabilization of PVC by epoxy compounds in which the latter reacts with HCl evolved at the early stages of dehydrochlorination of the polymer (Okieimen and Eromosele, 2000). Thus, the observed higher stabilizing effect of XSO relative to BSO in thermal degradation of PVC may be attributed to the presence of higher level of unsaturated fatty acids in the former. This is consistent also with the observed iodine value of XSO which is a factor of 1.5 higher than the value for BSO.

A test of the HCl trapping mechanism in PVC stabilization by oils can be seen from the results in Table 3 for thermo-oxidative degradation of the polymer in air at 190°C. From the t_{DH} and R_{DH} values, it is evident that PVC is not stabilized by XSO and BSO. Thus, in air,

Table 7. Thermal stability of oils, derivatives and PVC with additives.

| Sample(% wt loss)	Temperature for various extents of degradation (°C)					
	t_{max}(°C)	5%	10%	30%	50%	Temp. up to 200°C (% weight loss)
XSO	377.2	167.8	278.6	403.3	425.5	8.8
BSO	291.4	205.2	259.1	310.7	350.9	8.4
EXSO	393.0	307.2	351.5	412.6	432.0	5.6
EBSO	319.4	225.8	282.3	347.1	405.8	6.6
Additive to PVC						
None	298.0	234.9	275.9	308.6	330.0	
XSO 3 wt-%	308.0	277.6	294.6	319.1	343.0	
XSO 6 wt-%	310.0	279.0	296.2	321.4	343.4	
BSO 3 wt-%	305.6	265.4	290.4	316.3	338.9	
BSO 6 wt-%	309.0	269.5	292.4	319.5	342.8	
XSO/BSO (10/90) 3 wt-%	306.4	271.3	291.2	317.0	339.8	
XSO/BSO (50/50) 3 wt-%	306.9	265.1	291.8	318.8	340.7	
XSO/BSO(90/10) 3 wt-%	307.2	263.5	291.8	319.4	341.2	
EXSO 3 wt-%	312.5	282.7	298.3	323.1	347.4	
EBSO 3 wt-%	310.5	273.0	294.6	321.3	343.0	
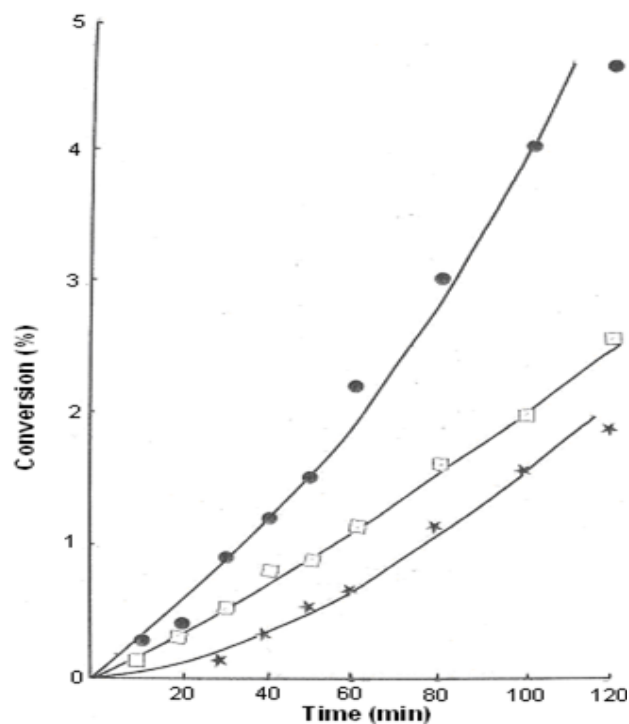
Figure 1. Thermal degradation of PVC under nitrogen in the absence of oils (·) 170 °C (□) 180 °C (●) 190 °C.

oxidative reactions of unsaturated fatty acids of the oils are dominant and are therefore rendered ineffective for trapping of HCl through addition reactions.

The oils were epoxidized and used for the degradation studies. Figure 2 represents the conversion plots for PVC degradation in the presence of 3 wt-% of the epoxidized
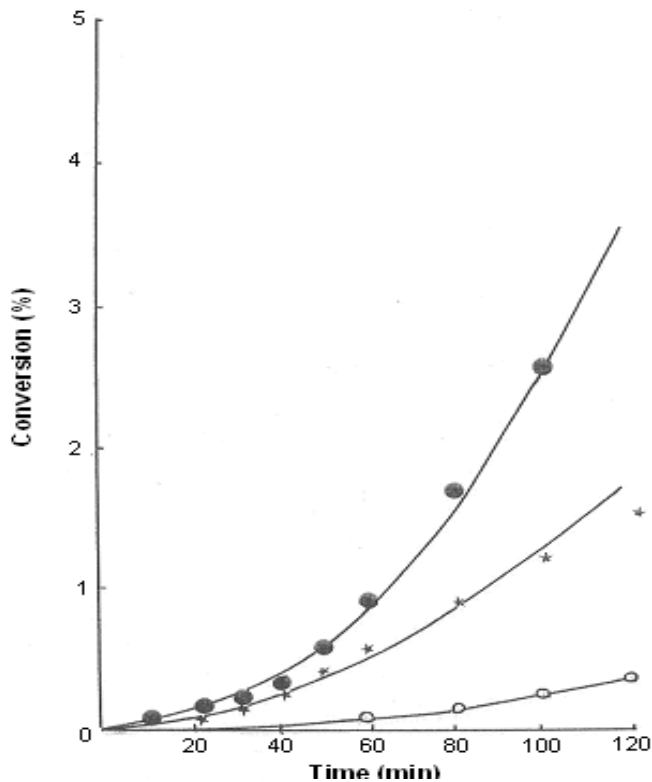
Figure 2. Thermal degradation of PVC under nitrogen in the presence of EXSO (○) 170°C (·) 180°C (●) 190°C.
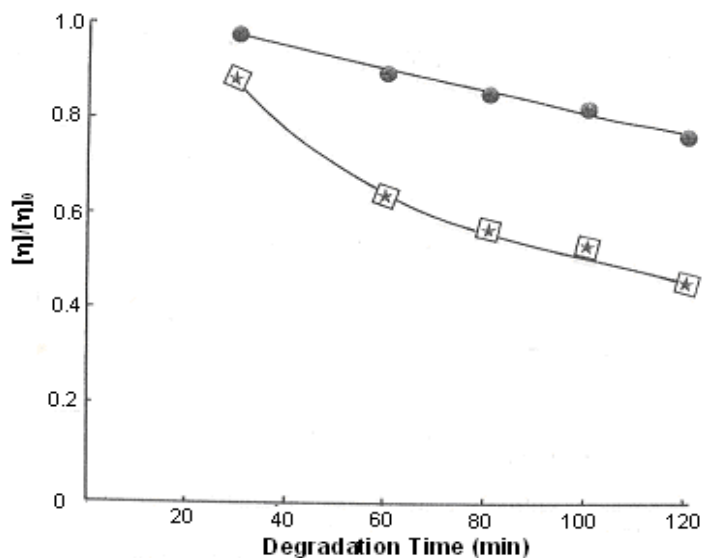
Figure 3. Plots of $[\eta]/[\eta]_0$ versus degradation time for PVC degraded under nitrogen in the presence of 3 wt% XSO and BSO at 170°C. No oil (·), 3 wt% BSO (□), and 3 wt% XSO (●).

oils, that is, EXSO. The t_{DH} and R_{DH} values for degradation at 180 and 190°C are shown in Table 4. From the latter, it is apparent that the epoxidized oil

derivatives show more stabilizing effect on PVC relative to the unmodified oils.

At 190°C, EXSO is a more effective stabilizer than
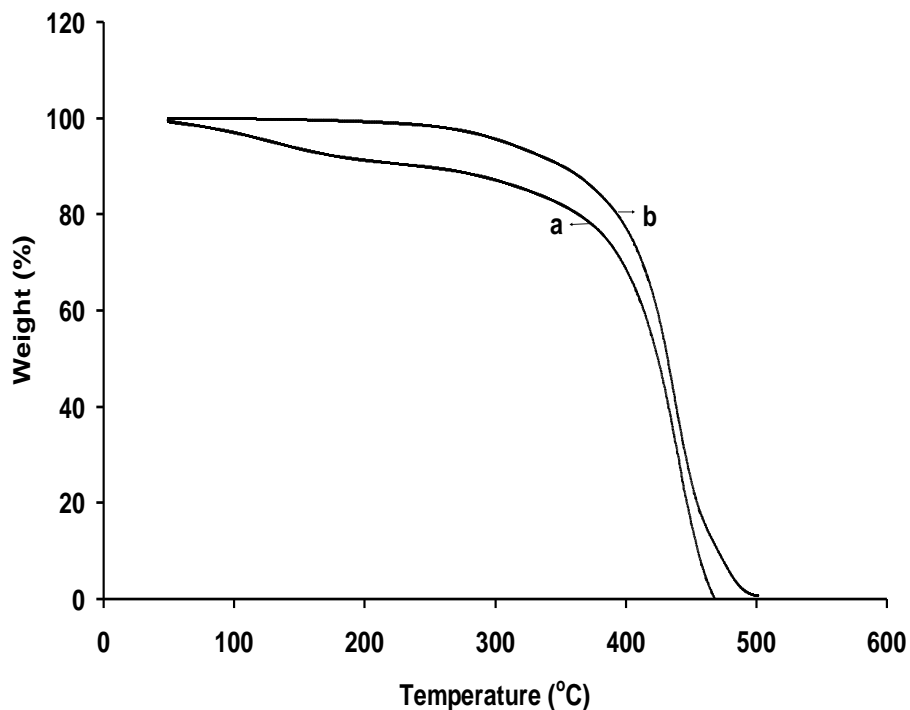
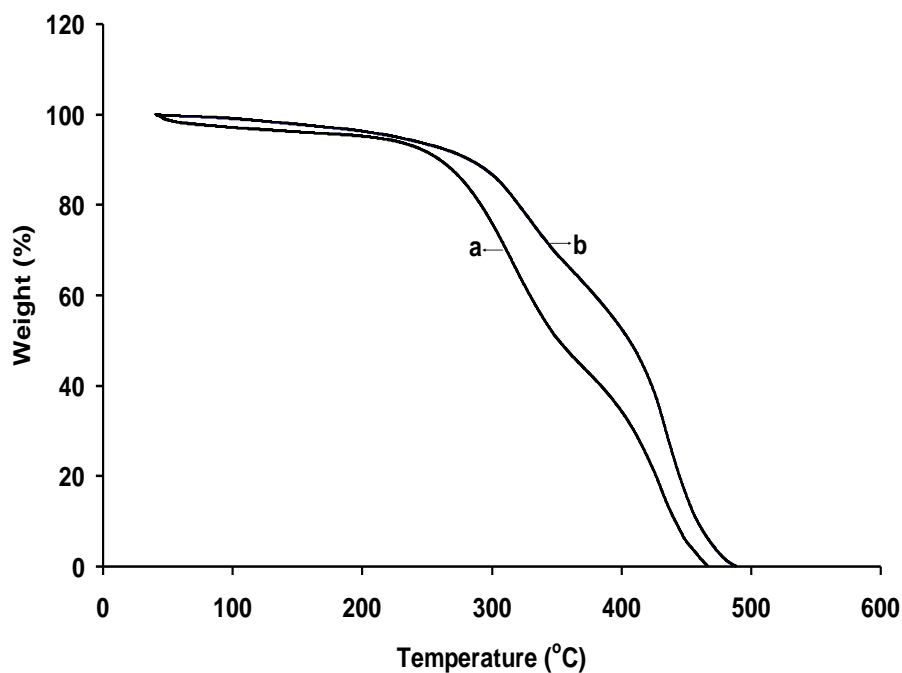**Figure 4.** Thermograms for (a) XSO and (b) EXSO (Residual wt %).

Figure 5. Thermograms for (a) BSO and (b) EBSO (Residual wt %).

EBSO by as much as 32% based on t_{DH} values. Thus, the order of stabilization of PVC by the oils and the epoxidized derivatives is: EXSO>EBSO>XSO>BSO. This order is corroborated by results of viscosity measurements of degraded PVC and from thermogravimetric studies. Figure 3 shows the plot of relative viscosity $[\eta]/[\eta]_o$ versus degradation time for PVC degraded under nitrogen in the presence of 3 wt-% XSO and BSO at 170°C.

It can be seen that the plots for 3 wt-% BSO and that of

PVC without additive are convergent and consistent with the results of kinetic studies which showed that BSO at this concentration was non-stabilizing. In both cases, the relative viscosity decreases with degradation time. Table 5 shows the viscosity parameters for PVC degraded at 190°C under nitrogen conditions. Four types of reactions may occur during thermal degradation of PVC, namely, dehydrochlorination, chain scission, crosslinking (Sogbaike and Okieimen, 2003) and oxidative reactions (Benavides et al., 2001) all of which may influence the viscosity of the polymer. In particular, the occurrence of conjugated polyene in PVC resulting from dehydrochlorination may confer on it rod-like properties and render it semi-flexible (Okieimen and Sogbaike, 1995) depending on the extent of reaction. From Table 5, the values for relative viscosity, $[\eta]/[\eta]_o$ are less than unity and suggest dominance of chain session in the degradation process. From the calculated percentage reduction in the values for intrinsic viscosity of degraded PVC samples, the order of stabilization of the oils and derivatives corroborates the one deduced from kinetic studies as mentioned previously. The activation energies, E_a for degradation of PVC under nitrogen atmosphere were calculated from the rate constant k_1, represented in Tables 2 and 4. The results are presented in Table 6. It can be seen that the activation energy for PVC degradation in the absence of additive is 79.76 kJmol^{-1}. In the presence of additives, the activation energy is much higher, with a value of 111.84 kJmol^{-1} for EXSO. The values for activation energy corroborate the order of stabilization of PVC by the oil and epoxidized derivatives as shown previously. The thermograms of the oils and their epoxidized derivatives are shown in Figures 4 and 5.

The thermograms exhibit a one-stage decomposition process and show that the oils are stable within the temperature range, 170 to 220°C normally encountered in processing of PVC. From the temperature at which maximum rate of degradation occurred, t_{max}, it is evident that epoxidation confers increased stability on the oils. The t_{max} for PVC in the presence of additives are shown in Table 7. The highest t_{max} of 312.5°C is seen for PVC with 3 wt-% EXSO and, for all the additives, the order of stabilization is EXSO>EBSO>XSO>BSO as earlier found. Furthermore, the t_{max} for PVC with 50/50 blend of XSO/BSO is intermediate in relation to the values for PVC incorporated with individual oils and suggests that the stabilizing effect of the blend is non-synergistic.

Conclusions

Poly(vinyl chloride) can be stabilized against thermal degradation under nitrogen atmosphere by *X. americana* seed oil, *B. aegyptiaca* seed oil, and their epoxidized derivatives. At equivalent weight concentrations, the order of stabilization is, EXSO> EBSO>XSO>BSO.

Thermal stabilization of PVC by the oils is attributable to trapping of HCl by addition reactions of the latter with unsaturated fatty acids. The higher stabilizing effect of XSO relative to BSO is consistent with higher iodine value of the oil and the presence of higher levels of unsaturated fatty acids in it. The effect of 50/50 blend of XSO/BSO in the stabilization of PVC under nitrogen atmosphere is non-synergistic. In air, PVC is unstabilized by XSO and BSO. This is adduced to dominant oxidative reactions of unsaturated fatty acids of the oils and consequent prevention of HCl-trapping addition reactions.

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