

Preparation of epoxidized sunflower oil metal soap derivatives and their use as heat stabilizers for polyvinyl chloride

Ouassila CHELIL^{1,2,*}, Naima BELHANECHÉ-BENSEMRA³, Daniel LÓPEZ GARCÍA⁴,
Marta FERNÁNDEZ-GARCÍA⁴, Mohamed Tahar BENANIBA¹

¹Laboratory of Multiphase Polymeric Materials, Department of Process Engineering, Faculty of Engineering, Ferhat Abbas University, Sétif, Algeria

²Department of Process Engineering, Faculty of Engineering, University of 20 Aout 1955, Skikda, Algeria

³Laboratory of Environmental Sciences and Techniques, Ecole Nationale Polytechnique, El-Harrach, Algiers, Algeria

⁴Institute of Science and Technology of Polymers (ICTP-CSIC), Madrid, Spain

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Abstract: The aim of this work was to prepare metal soaps of epoxidized sunflower oil (ESO) and use them as thermal stabilizers for polyvinyl chloride (PVC). For that purpose, commercial sunflower oil was first epoxidized and then used to prepare (Ba, Zn, Pb, and Cd) metal soap derivatives, which were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The prepared metal soaps derivatives of ESO were used as thermal stabilizers for plasticized PVC. Discoloration, residual thermal stability at 200 °C, and rheological properties of PVC samples were tested. The structural modifications were investigated by UV-visible spectroscopy. The best thermal stabilization effects were observed in the presence of Pb soap of ESO. Furthermore, metal derivatives of ESO were classified according to their stabilizing effect as follows: Pb-ESO > Ba-ESO > Cd-ESO > ESO > Zn-ESO.

Key words: PVC, metal soap epoxidized sunflower oil derivatives, thermal stabilization, rheology, TGA, DSC, UV-visible

1. Introduction

Polyvinyl chloride (PVC) is the most commonly used amorphous polymer because of its good characteristics such as light weight, durability, and excellent water, biological, flame, and chemical resistances.¹ However, PVC is considered to be one of the least stable polymers to heat² and to UV rays.³ Heat and UV rays are well known to be the most active agents of degradation.⁴ Dehydrochlorination, being the obvious result of this type of degradation, leads to problems of polymer structure change and brownish coloring.⁵

Thermal degradation of PVC is due to irregular structures responsible for the formation of labile chlorine atoms. Hydrochloric acid (HCl) release is observed when the polymer is heated at 80 °C, whereas its processing temperature range is 180 °C to 200 °C.⁶

It is well known that plasticized PVC undergoes degradation with increasing temperature in a process called dehydrochlorination, elimination of HCl with creation of conjugated double bonds, followed by a color change of the polymer that varies from yellow to orange red, brown, and finally black.^{7,8} Under the effect of a source of energy (mechanical, thermal or light), the labile chlorine will evolve as HCl, giving way to a double

*Correspondence: chellil_wassila@yahoo.fr

bond located in the alpha position of the chlorine. This chlorine, once in the allylic position, is particularly unstable and causes both a rapid elimination of another HCl molecule and the formation of a conjugated double bond.⁹

To overcome the weak thermal stability of PVC, the use of heat stabilizers is required.^{10,11} The stabilizers must not only fix HCl but also act in such a way that they are able to eliminate the polyenic sequences or their chromophoric character to reduce the blackening of the polymer.¹²

Thermal stabilizers are basic additives for PVC in technological processing. The role of different types of stabilizers is to bond the eliminated hydrogen chloride, replace the labile chlorine atoms in the polymer chain thus preventing further dehydrochlorination, reduce the length of the arising polyene sequences, preserve the coloring of the polymer, or to protect the polymer from the catalytic effect of stabilizer decay on dehydrochlorination.¹³

The incorporation of heat stabilizers in PVC allows work at high temperatures.⁴ Additives that have found practical applications as thermal stabilizers for PVC include metal soaps of organic acids, organometallic compounds, and chain reaction inhibitors.^{14,15} Among the thermal stabilizers, metal soaps derived from epoxidized oils are used.^{10,11,16}

In previous works, epoxidized sunflower oil (ESO) has been used as a thermal stabilizer for PVC in the presence of metal carboxylates.^{17,18}

The aims of the present work were to prepare, characterize, and study the effects of Ba, Zn, Pb, and Cd metal soaps of ESO on thermal degradation of PVC. Stabilized PVC formulations with ESO metal soap derivatives were prepared and characterized.

Although the toxicity of some metals, including cadmium and lead, is recognized even at very low concentrations and phthalates are on the list of "substances of very high concern",^{19–21} the objective of the present work was to gain knowledge about the thermal stabilization effects of various metal soap derivatives of ESO on plasticized PVC and to compare the behavior of the formulations based on the prepared thermal stabilizers. It is obvious that according to actual limitations and restrictions on the use of PVC including phthalates,²¹ ESO and Zn soap derivative of ESO are candidates for future applications as thermal stabilizers and plasticizers.

2. Results and discussion

2.1. Characterization of metal soaps of ESO

2.1.1. FTIR spectroscopy analysis

The spectra obtained for Ba, Zn, Pb, and Cd soaps derived from ESO (Figures 1a–1d, respectively) showed differences in the zone of hydroperoxides and hydroxyl groups ($3600\text{--}3200\text{ cm}^{-1}$) and a similarity in the zone of carbonyl groups ($1800\text{--}1500\text{ cm}^{-1}$), ester groups ($1700\text{--}1690\text{ cm}^{-1}$), conjugated double bonds ($1690\text{--}1620\text{ cm}^{-1}$),²² COO^- groups,²³ and oxirane groups ($960\text{--}810\text{ cm}^{-1}$). As can be seen in Figure 1, the absence of a OH bond vibration ($3600\text{--}3140\text{ cm}^{-1}$) is quite clear in the spectra of barium soap, lead soap, and cadmium soap, whereas the spectrum of zinc soap shows a band due to the stretching vibration of OH in the range of $3600\text{--}3200\text{ cm}^{-1}$, observed as a broad band centered at 3296 cm^{-1} . Two intense peaks observed at 1548 and 1400 cm^{-1} and attributed to ($\nu_s\text{COO}^-$ and $\nu_a\text{COO}^-$) symmetric and asymmetric stretching modes were defined to correspond to the values reported in the literature for zinc stearate.^{16,24,25} The position of the first band was determined by the bound cation and was observed at 1510 , 1526 , 1538 , and 1538 cm^{-1} for barium,

zinc, lead, and cadmium soaps of ESO, respectively. These results are almost the same as those observed by Okieimen et al.²³

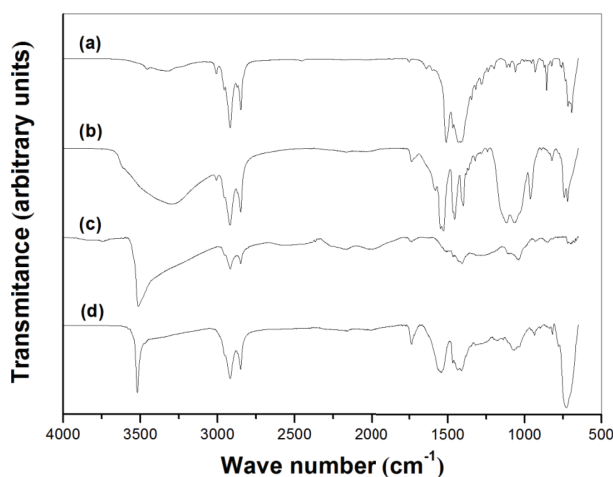


Figure 1. FTIR spectra of epoxidized sunflower oil metal soap derivatives: (a) Ba-ESO, (b) Zn-ESO, (c) Pb-ESO, (d) Cd-ESO.

The other groups observed at approximately 2916, 2845, and 1460 cm^{-1} correspond to the asymmetric, symmetrical, and methylene scissoring modes ($\nu_a \text{CH}_2$, $\nu_s \text{CH}_2$, and $\nu_s \text{CH}_2$) because of the alkyl group present in the structure of ESO. The IR spectra indicate the appearance of a band between 1745 and 1750 cm^{-1} , corresponding to the elongation vibration of free esters ($\text{C}=\text{O}$) of the oil,¹¹ an absorption band at about 820 cm^{-1} attributed to the vibration of oxirane cycle,²⁶ and a peak located between 1340 cm^{-1} and 1200 cm^{-1} due to the stretching of $\text{Zn}-\text{CH}_3$.²²

2.1.2. Thermal characterization

Thermogravimetric (TG) and dynamic thermogravimetric (DTG) curves of ESO and metal soaps Ba, Zn, Pb, and Cd of ESO are shown in Figures 2 and 3, the corresponding data being given in Table 1. This test allowed identification of the main phases of degradation of metal soaps at high temperatures. The decomposition steps are particularly well represented by the signal of the derivative.²⁷

Table 1. TG data of ESO and metal soap derivatives of ESO.

Samples	t_{d1} ($^{\circ}\text{C}$)	T_{dmax} ($^{\circ}\text{C}$)	Mass loss (%)	Residue (%) at 500 $^{\circ}\text{C}$
ESO	-	323.93	99.2	0.8
Barium soap of ESO	247.18	462.40	17.5	82.5
Zinc soap of ESO	243.98	413.90	58.0	42.0
Lead soap of ESO	284.21	491.74	14.0	86.0
Cadmium soap of ESO	245.48	437.96	40.0	60.0

t_{d1} : Onset of degradation.

T_{dmax} : Maximum degradation temperature.

The stabilizing effect was clearly observed up to a heating temperature value, beyond which mass loss was noted to increase with increasing temperature (residual mass).

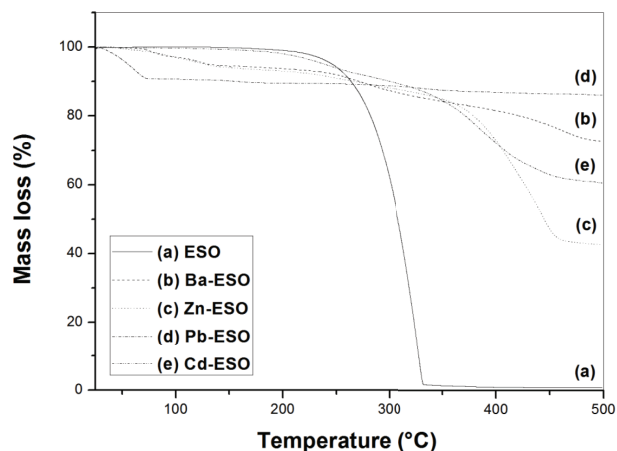


Figure 2. TG curves for ESO and different metal soaps of ESO.

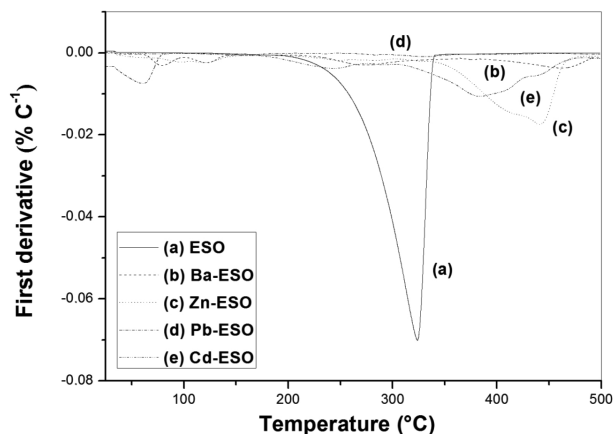


Figure 3. DTG curves for ESO and different metal soaps of ESO.

Analysis of the DTG curves showed the appearance of three main zones of mass loss (Table 1). The first zone, observed at about 100 °C, can be attributed to the loss of water as observed in previous studies.^{23,28}

The second zone, ranging from 200 °C to 350 °C, was due to both volatilization of ESO (Figures 2 and 3) and the beginning of degradation of metal soaps (Ba, Zn, Pb, and Cd), noted as t_{d1} .

In addition, two shoulders were observed at 243 °C and 291 °C for zinc and cadmium soaps, probably corresponding to the loss or degradation of the ESO and stabilizer.

According to t_{d1} values, the different soaps were classified according to the following descending order of stabilizing efficacy: Pb-ESO > Ba-ESO > Cd-ESO > Zn-ESO. The most stable soap is lead soap, followed by barium soap.²⁹

To be effective in stabilizing a polymer against thermal degradation, the additive should be stable within the processing temperature range of the polymer.^{23,28} In our study the metal soaps were thermally stable up to 200 °C (Figures 2 and 3) and the mass loss was about 6.97%, 9.90%, 2.15%, and 8.64%, respectively, for barium, zinc, lead, and cadmium soaps of ESO.

In the third zone, ranging from 350 °C to 500 °C, the mass loss must be due to the degradation of metal soaps, which was noted as T_{dmax} .

On the other hand, the residual thermal stabilities of various formulations were classified according to the following decreasing order of efficacy: Pb-ESO > Ba-ESO > Cd-ESO > Zn-ESO.

2.1.3. Differential scanning calorimetric analysis

The phase transitions and thermal behavior of metal soaps of ESO were studied by differential scanning calorimetry (DSC). These soaps are in solid state at room temperature. The DSC curves of ESO and metal soap derivatives of ESO during heating cycles are represented in Figure 4 and the corresponding data are given in Table 2. According to the thermogram of ESO, the temperature to the top of the endothermic peak corresponds to the melting temperature of ESO while heating; one or more phase transitions may be observed over the temperature range up to the onset of thermal decomposition.

These results are in good agreement with those found when studying the thermal behavior of zinc soap of rubber seed oil.¹¹

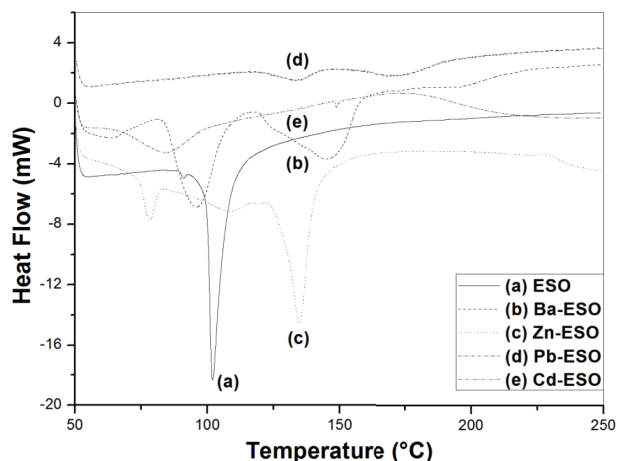


Figure 4. DSC curves of ESO and different metal soaps of ESO.

Table 2. DSC results of ESO and metal soap derivatives of ESO.

Samples	T_{m1} (°C)	T_{m2} (°C)
ESO	100.0	-
Barium soap of ESO	96.21	145.80–195.84
Zinc soap of ESO	78.45	134.65
Lead soap of ESO	134.95	172.07
Cadmium soap of ESO	84.42	148.83

T_{m1} : Volatilization of ESO.

T_{m2} : Initial decomposition of metal soaps.

Two distinct melting temperatures were clearly observed in Figure 4. The first (T_{m1}), between 78 and 130 °C, could be due to evolution of H_2O in soaps on heating or due to solid–solid phase transitions, while the second (T_{m2}), from 145 to 195 °C, is due to the first decomposition of metal soaps.

2.2. Characterization of PVC films

2.2.1. Discoloration analysis

The discoloration of PVC films can be explained by the release of HCl and the formation of long polyenic sequences. A remarkable absence of initial coloration of PVC samples stabilized with ESO and its metal soap derivatives was observed. The coloration evolution scheme of the different samples is shown in Table 3. The same degree of coloration was observed for all the tested thermal stabilizers.

Table 3. Discoloration of different samples.

Samples	Degree of coloration
PVC/ESO	1
PVC/Ba-ESO	1
PVC/Zn-ESO	1
PVC/Pb-ESO	1
PVC/Cd-ESO	1

2.2.2. Residual thermal stability of PVC films

Residual thermal stability gives information on the amount of active thermal stabilizer in the analyzed samples. Globally, Figure 5 showed that the residual thermal stability of Pb soaps was higher than that of Ba, Zn, and Cd soaps.

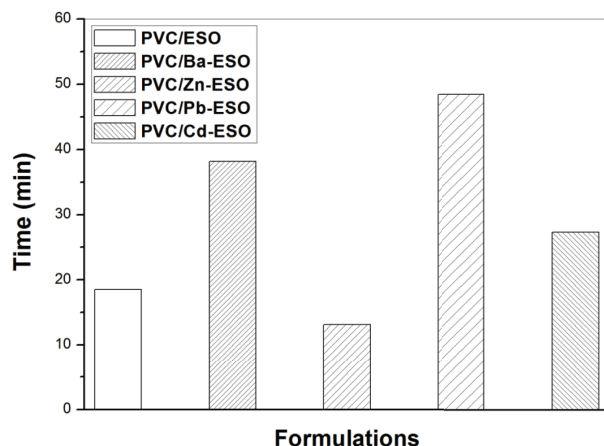


Figure 5. Variation in thermal stability of different formulations.

2.2.3. UV-visible spectroscopy

Figure 6 represents the UV-visible spectra of the different formulations from 205 to 400 nm. These spectra show that all polyenes formed absorb in the region below 300 nm. The maxima are located at 222 nm, 245 nm, and 278 nm, for all formulations. These polyenes contain a number of conjugated double bonds less than or equal to 4 (medium sequences).³⁰

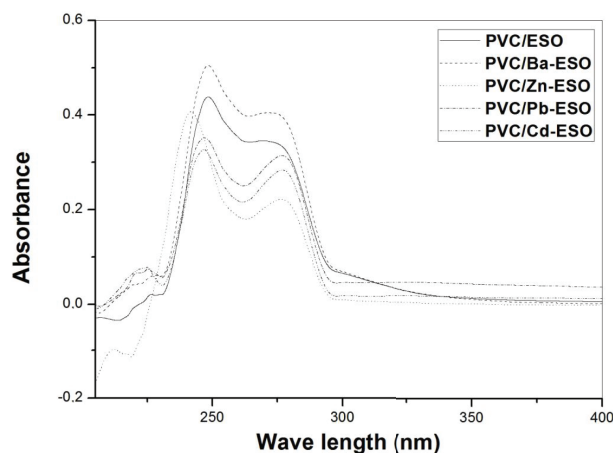
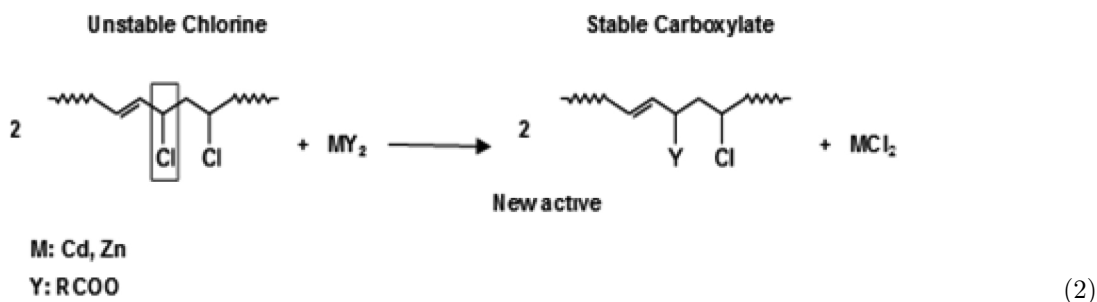


Figure 6. UV-visible spectra of PVC stabilized with ESO and different metal soaps of ESO.

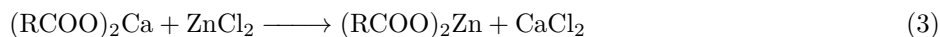
The coloration has been ascribed to the formation of polyene sequences long enough to absorb in the visible region, i.e. a length exceeding five units.³¹ Hence, the remarkable absence of initial coloration of the PVC samples stabilized with ESO and its metal soaps derivatives is attributed to the formulation of short polyene sequences.

The oxirane ring is a well-known acid acceptor in PVC. HCl released from initial degradation was scavenged by ESO, converting the epoxy group to chlorohydrins. It has also been suggested that the epoxy ring might act as a polyene blocker, opening by reaction at a labile hydrogen site in the PVC to form an ether linkage with the chlorinated epoxy.^{17,32}

The role of barium, cadmium, calcium, and zinc salt-based stabilizers is to catch HCl released by the polymer (reaction 1), replace the labile chlorines (reaction 2), and reduce the color of degraded polymer.⁹ These stabilizers were efficient at the beginning of PVC thermal treatment, but once completely consumed a rapid increase in HCl release was noted with a coloration of the polymer.³³ This was probably due to the catalytic effect of CdCl₂ or ZnCl₂ on the thermal degradation of PVC.¹²



The zinc or cadmium chloride formed (catalyst of DHC of PVC, as all Lewis acids) was neutralized by reacting with calcium or barium carboxylates (reaction 3). The carboxylates could be stearates, laureates, phenates, and benzoates.^{17,34}



Lead-based stabilizers were proved to be effective thermal stabilizers for PVC because of their good dispersion in the polymer.³⁵ Their action mechanism is illustrated in Scheme 1. The most important representative is lead stearate $Pb(C_{17}H_{35}CO_2)_2$.

2.2.4. Rheological properties

A rheological study in static pattern at 180 °C and 190 °C was performed to investigate the nature of the flow of PVC formulations stabilized with metal soaps of ESO. As shown in Figures 7a and 7b, shear stress increased with shearing. The opposite phenomenon was observed in the case of apparent viscosity (Figures 7c and 7d). These features are directly related to reticulation. On the other hand, for the same shear rate, the shear stress and apparent viscosity obtained in the case of PVC stabilized with Pb soap were higher than those corresponding to PVC stabilized with Ba, Zn, and Cd soaps. In all cases, the nature of the flow was pseudoplastic.³⁷

2.3. Conclusion

The present study focused on the preparation and characterization of barium, zinc, lead, and cadmium soaps from ESO for their use as heat stabilizers. The results obtained showed a notable absence of initial coloration of PVC samples stabilized with ESO and its metal soap derivatives due to the formation of short polyenes

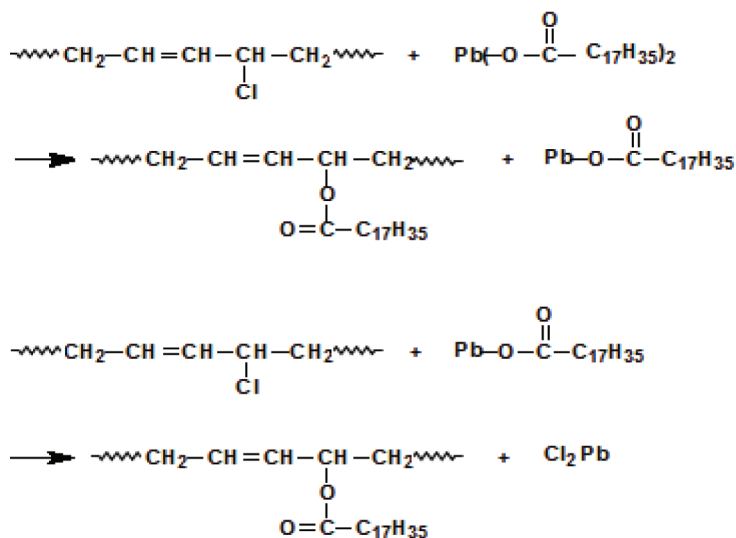
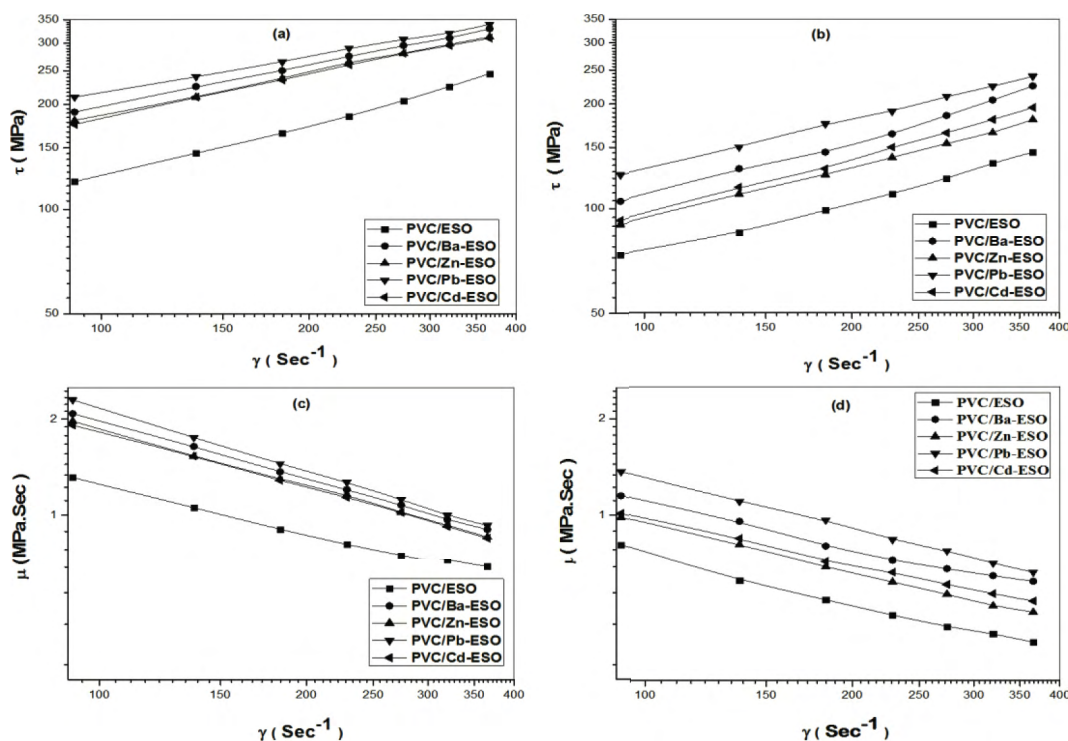
Scheme 1. Reaction mechanism of lead-based stabilizers on PVC.³⁶

Figure 7. Variation in rheological properties of PVC formulations as a function of shear rate (γ): (a) shear stress (τ) at 180 °C; (b) shear stress (τ) at 190 °C; (c) apparent viscosity (μ) at 180 °C; (d) apparent viscosity (μ) at 190 °C.

containing a number of conjugated double bonds less than or equal to 4 (medium sequences). The best thermal stabilization effects were observed in the presence of ESO Pb soap. Furthermore, the order of efficacy of ESO metal derivatives is as follows: Pb-ESO > Ba-ESO > Cd-ESO > ESO > Zn-ESO.

Finally, the rheological results showed that, in all cases, the nature of the flow was pseudoplastic.

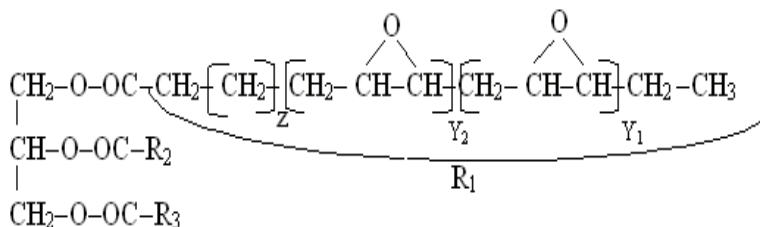
3. Experimental

3.1. Materials

An Algerian PVC (4000 M) with a K value of 65–67, a polymerization degree of 970–1070, and an apparent density of 0.5–0.54 g mL⁻¹ was used. Dioctyl phthalate plasticizer (DOP) (Palatinol AH-L supplied by BASF, density = 0.98 g cm⁻³) and the lubricant stearic acid (produced by BASF) were used. The sunflower oil was a commercial product used to prepare ESO. BaCl₂.2H₂O, ZnSO₄, Pb(NO₃)₂, and Cd(NO₃)₂.4H₂O (supplied by Sigma-Aldrich) were used as received.

3.2. Epoxidation of sunflower oil

Liquid ESO (Scheme 2) was prepared as described previously.³⁷ The epoxidation level was measured according to AOCS Cd 9-57 standard.³⁸ The oxirane oxygen level was 5.2%.



Scheme 2. Chemical structure of epoxidized sunflower oil.¹⁷

Here R₂ and R₃ are unsaturated fatty acid chains that may be identical to or different from R₁ in terms of the number of epoxy groups present.

3.3. Preparation of metal soaps of ESO

Metal soaps of ESO were prepared as described by Burrows et al.³⁹ The ESO (9.2 g) was dissolved in 50 mL of hot ethanol and treated with 20 mL of 20% (w/v) sodium hydroxide solution. To this mixture was slowly added 100 mL of 30% (w/v) aqueous solution of the metal salt with continuous stirring. The precipitated soap was washed with hot water and air-dried. The soaps were prepared using BaCl₂.2H₂O, ZnSO₄, Pb(NO₃)₂, and Cd(NO₃)₂.4H₂O.²³

3.4. Characterization of metal soaps of ESO

3.4.1. Fourier transform infrared spectroscopy

Powders of metal soaps and additives (stearic acid, BaCl₂.2H₂O, ZnSO₄, Pb(NO₃)₂, and Cd(NO₃)₂.4H₂O) were pellet-like shaped with KBr at 14 t cm⁻² pressure before being analyzed. FTIR spectra of the different soaps were recorded using a PerkinElmer 1000 apparatus at a resolution of 2 cm⁻¹ and the number of scans was 16. DOP and ESO were analyzed in solution state.

3.4.2. Thermogravimetric analysis

The thermogravimetric analysis was performed on a thermobalance Mettler Toledo type TGA/SDTA851, in the temperature range of 25 °C to 500 °C, under a nitrogen flow of 40 mL min⁻¹, and with a heating rate of 10 °C min⁻¹.

3.4.3. Differential scanning calorimetry

Conventional differential scanning calorimetric measurements from 50 °C to 250 °C were recorded using a TA Instruments DSC Q2000 with an intracooler for low temperatures. The temperature scale was calibrated from the melting point of high purity indium. Samples weighed with a PerkinElmer AD4 electronic autobalance were scanned at 10 °C min⁻¹ under dry nitrogen (30 mL min⁻¹).

3.5. Preparation of PVC films

The samples were prepared using the following amounts: 100 g of PVC stabilized by 5 g of ESO, 1 g of stearic acid as lubricant, 35 g of DEHP as plasticizer, and 3 g of ESO metal soaps. The films were prepared in a two-roll mill at 170 °C over 10 min.

3.6. Characterization of PVC films

3.6.1. Residual thermal stability of PVC films

The residual thermal stability was evaluated according to the thermal stability determined by the change in color of PVC.⁴⁰ The method consists of putting a sample (0.5 g) of PVC in a sealed test tube and the set is immersed into an oil bath heated at 200 °C. The appearance of color indicates that HCl is released due to thermal degradation. A change in the color of the PVC sample from opaque white to brown to black was observed. The time required for the appearance of the color is associated with the residual thermal stability.

3.6.2. Discoloration analysis of PVC films

The evolution of discoloration was measured using a 10-degree color scale (Synmero) as described by Ocskay et al.⁴¹

3.6.3. UV-visible spectroscopy of PVC films

UV-visible spectra of PVC purified samples in distilled THF ($C = 2 \text{ g L}^{-1}$) were obtained using a PE UV SPECTRUM ASCII PEDS 1.60 spectrophotometer. The polymer was purified by two-cycle dissolution in THF, precipitation with methanol, and filtration. The released powder was dried for 24 h at room temperature and then used to prepare the solutions of purified PVC in distilled THF.

3.6.4. Rheological properties of PVC films

Apparent viscosity and shear stress were determined using a capillary rheometer (CONTROLAB model 102 COP 10), using the following working conditions: temperature 180 °C and 190 °C, piston diameter D_p 20 mm, and piston linear speed 10–40 mm min⁻¹.

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