Evaluation Effects of Biobased Plasticizer on the Thermal, Mechanical, Dynamical Mechanical Properties, and Permanence of Plasticized PVC

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ABSTRACT: Sunflower oil (SO) is a renewable resource that can be epoxidized, and the epoxidized SO has potential uses as an environmentally friendly in polymeric formulations, especially for poly (vinyl chloride) (PVC). Epoxidized sunflower oil (ESO) was prepared by treating the oil with peracetic acid generated in situ by reacting glacial acetic acid with hydrogen peroxide. Epoxidation was confirmed using spectroscopic and titration methods. ESO was used as a coplasticizer in PVC for the partial replacement of di-(2-ethyl hexyl) phthalate (DEHP). The effect of ESO on the thermal stability of plasticized PVC was evaluated by using synmero scale for the sheets. In presence of ESO plasticized PVC samples showed a reduction in discoloration and the number of conjugated double bonds. By using thermogravimetry, the incorporation of 15/45 of ESO/DEHP in PVC presents the lowest weight loss. The results of the shore hardness and mechanical properties showed that a proportion of DEHP could be substituted by ESO. By use of DMA, the formulation which contains 25 % wt of ESO in plasticizer system shifts the glass transition temperature (T_g) to ambient temperature. The migration phenomenon was studied on PVC based samples plasticized with DEHP and ESO in varying amounts. The migration was monitored by the weight loss percentage of the samples immersed into n-hexane or heated in an oven. The amount of extracted or volatilized DEHP is proportional to the added ratio of ESO in plasticizer system. All of this favored the partial replacement of DEHP by ESO as biobased plasticizer for flexible PVC. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3499–3508, 2010

Key words: PVC; plasticizer; DEHP; poxidized sunflower oil; mechanical properties; T_g

INTRODUCTION

The use of plasticizers is one of the most efficient ways to modify the thermal and mechanical properties of polymers. Plasticizers are often low-molecular weight compounds that lower the glass transition temperature (T_g) and convert rigid polymers into flexible ones. To be effective, a plasticizer must distribute itself between the polymer chains and interact with functional groups, thereby by reducing the interaction between the polymer chains and softening the matrix.[1] Most of plasticizers are high boiling organic liquids, and their function is to reduce the T_g of the plastics to a level below the temperature used in the actual application of the plastics. Because of the brittle nature of the neat PVC, it is often compounded with plasticizers to enhance its flexibility and toughness for various applications, and the most commonly used plasticizers for PVC are phthalate. Since di-(2-ethyl hexyl) phthalate (DEHP) was introduced in the 1930s, it has been the most widely used plasticizer. However, it is known that conventional low-molecular weight organic plasticizers for PVC, such DEHP, are somewhat volatile, leading to plasticizer loss and unwanted deterioration of the material properties over the course of time.[2,3] Phthalic plasticizers and metal soap stabilizers are usually used with epoxides as costabilizers and heat stabilizers in PVC; they have been classified as epoxy plasticizers.[4,5]

In our previous studies,[6-8] we examined the effect of epoxidized sunflower oil (ESO) on the thermal degradation of PVC by using dehydrochlorination rate measurement. Several other reports[9,10] on the use of epoxidized triglycerides as heat stabilizing additives for PVC claim that their effectiveness as stabilizers is related to the oxirane content and is because of the facile reactions of the epoxide with HCl evolved at the early stages of the dehydrochlorination (which precludes autoacceleration of the dehydrochlorination process) and with the labile chlorine atoms in the PVC (which reduces the

susceptibility of the polymer to dehydrochlorination). The suitability of epoxidized triglycerides as biodegradable nontoxic plasticizers for PVC provides additional rationales for the examination of the effect of epoxidized triglycerides on the plasticization of PVC formulations.

In this study, we explored the possibility of using a combination of ESO and DEHP as the plasticizer for PVC. The thermal, mechanical, dynamical mechanical properties, and leaching of plasticizer system were examined.

EXPERIMENTAL PART

Materials and equipment

The formulations used were based on PVC, produced by the Algerian company ENIP-Skikda, with the following physical characteristics: grade = 4000 M, K value= $65 - 67$, density (powder PVC) = 0.48 $- 0.56$. The other ingredients added to the PVC resin were DEHP, with a viscosity of 80 MPa.s and a molecular weight of 390 g mol^{-1}; Ca/Zn based carboxylate used as thermal stabilizer, and stearic acid, used as an external lubricant.

ESO was especially prepared. All analytical grade solvents were used as obtained from Prolabo (Paris, French). PSK 1411 cross-linked poly (styrene-sulfonic acid) ion exchange resin and hydrogen peroxide (30%) were purchased from Bayer (Munich, Germany) and Aldrich (Lyon, French) Chemicals, respectively.

Preparation of ESO

Synthesis of ESO

For the synthesis of ESO, a solution of sunflower oil (SO) (100 g, 0.113 mol), glacial acetic acid (20.4 g, 0.34 mol), PSK 1411 (21 g), and toluene (40 g) were placed in a 500 mL four-neck round flask equipped with mechanical stirrer, thermometer sensor, and reflux condenser. The mixtures were heated and the temperature was maintained at 55°C. Then 30% H_2O_2 (79.4, 0.7 mol) were added slowly to a separator funnel and reacted at 55°C for 7 h. After the reaction was completed, the crude product was filtered and washed with distilled water repeatedly until pH was 7. The oil phase was dried with anhydrous sodium sulfate and then filtered. Finally, the toluene was removed in a vacuum oven at 80°C. The yield of the obtained ESO was 90%. The level of epoxidation (6.4% oxirane oxygen) was determined using analytical method.[11]

Formulation blending

The DEHP and ESO are 60 phr to PVC. The effect of ESO on the various properties of PVC/plasticizer
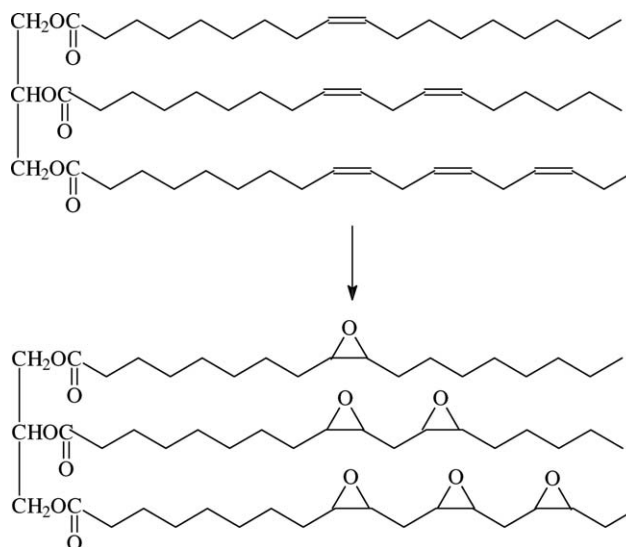
Scheme 1 Epoxidation of vegetable oil.

(100/60), with the plasticizer made up of (ESO/ DEHP) is studied on 00/60, 55/05, 50/10, 45/15, 40/20, 25/35, and 30/30 weight ratios of ESO/ DEHP. The PVC used in all blends contained a Ca/ Zn = 1 wt % of thermal stabilizer to minimize degradation. The blends were processed into sheets on roll-mill for 10 min with the rolls set at a temperature of 170°C, roll friction ratio of 1.25. The sheets were compression molded to make films and plaques, which were required for some of the tests. The operating temperature was 170°C for 3 min with hydraulic pressure of 20 tons.

Characterization methods

^{1}H NMR of SO and ESO

^{1}H NMR data of ESO were recorded using a Bruker AM 300 spectrometer, operating at 500 MHz using a 5-mm broadband inverse Z-gradient probe in CDCl$_3$.

Discoloration analysis

The evolution of discoloration was measured using a ten-degree color scale synmero as described by Ocskay et al.[12] Changes in the discoloration degrees were determined for the sheets obtained on roll-mill and after heat treatment in air circulating oven at 100°C for 7 days.

UV-visible analysis

The PVC materials with different components were pressed into films with the thickness about 100 μm. UV-visible spectra of films PVC were obtained by using a Shimadzu 120-02 UV-visible spectrophotometer.
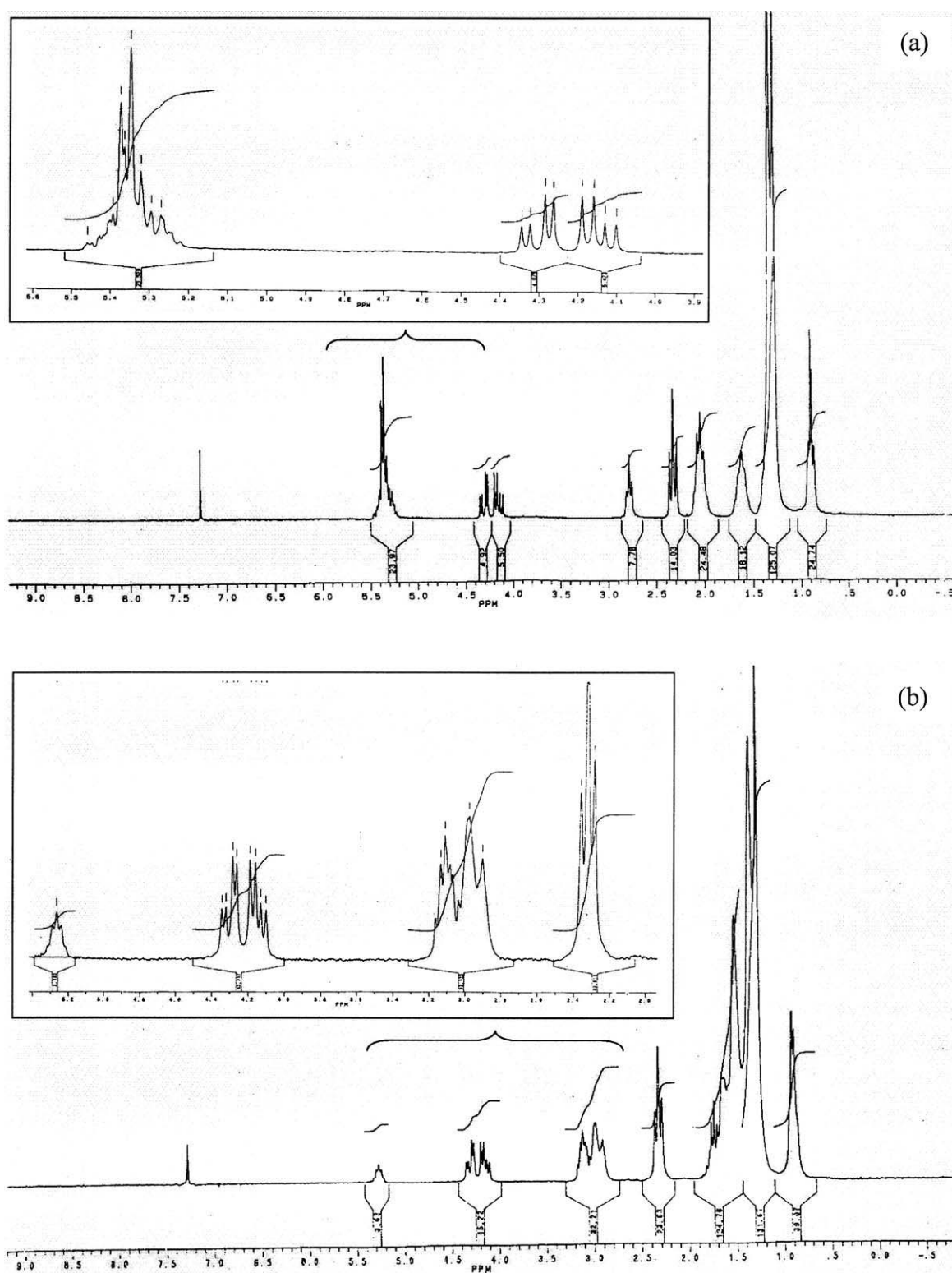
Figure 1 1H NMR spectra of SO (a) and ESO (b).

Thermogravimetric studies

Thermogravimetric (TG) analysis was performed on the polymeric formulations by using an ATG (Q500) instrument. The samples ranging between 10 and 15 mg were heated under air flow (90 mL min^{-1}) from room temperature to 600°C with a heating rate of 10°C min^{-1}. The results presented here were reproducible and the temperature and mass loss deviations were within the maximum range of ± 2 %.
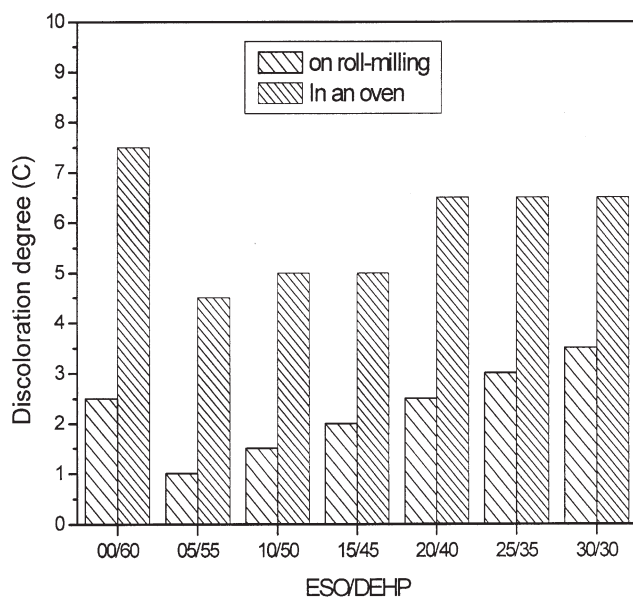
Figure 2 Discoloration degrees of PVC sheets obtained by heat treatment on two rolls milling at 170°C for 10 min and in oven at 100°C for 7 days.

Hardness

The shore A and D hardness test was carried out according to ISO 7619 using a Zwick 7206 hardness tester. This method is based on an indenter penetration test and requires a sample thickness. Ten measurements were made on each sample type.

Mechanical properties

The young modulus, tensile strength, and elongation at break were determined from a traction test in a universal dynamometer Instron. Samples were tested at room temperature, using a 0.5 KN load cell, with a testing speed of 20 mm min^{-1}.

Dynamic mechanical analysis

The thermomechanical behavior of the formulations was characterized using TA instruments DMA 2980 over a temperature range from −100 to 150°C with a 2°C per minute heating rate at a frequency of 1 Hz. Samples with a large of 5 mm and a length of 15 mm were tested in the single cantilever mode in DMA with a fixed displacement. Storage modulus and loss modulus were measured as function of temperature.
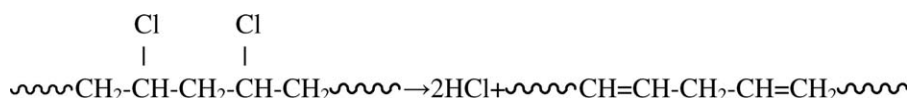
Migration and extraction of plasticizer

Extraction of plasticizer from the blends was examined in n-hexane at 40°C under stirring for a month. 15 mm × 15 mm × 1 mm samples were pre-weighted and immersed into 50 mL of methanol in the flask and was shaken occasionally. After the extraction, the samples were fully dried in reduced pressure until the weight of the samples was constant. The weight of the extractable part was calculated.

Samples of PVC sheets were heated in an air circulating oven 100°C for 7 days. Changes in weights and discoloration degrees were measured after heat treatment. Each sample was taken off and weighted. The rate variation of the mass was determined as a function of time following the relation:

$$\tau = (m_t - m_0/m_0) \times 100 \qquad (1)$$

where m_0, is initial mass before immersion and m_t, is mass of the sample at the time t.

m and m_0 were measured to an accuracy of 10^{-4} g.

RESULTS AND DISCUSSION

Our study investigates the suitability of ESO as a PVC coplasticizer. Epoxidation is the addition of an oxygen atom to a carbon-carbon double bond to form a 3-membered ring with epoxide (or oxirane) functionality. The unsaturated double bonds of SO may be used to introduce functional groups like epoxides. Scheme 1 shows an example of a typical epoxidation product of oil.

From the spectra given in Figure 1(a,b), ^{1}H NMR measurement on ESO (6.4% oxirane oxygen) shows the disappearance of the signals of vinylic protons at 5.3–5.5 ppm and indicates that the epoxy group is present in the δ 3.0–3.2 ppm region. The methine proton of ─CH$_2$─CH─CH$_2$ backbone at δ 5.1– 5.3 ppm, methylene proton of ─CH$_2$─CH─CH$_2$─ glycerol's backbone at δ 4.0–4.4 ppm, CH$_2$ proton adjacent to two epoxy group at δ 2.8–3.0 ppm, ─CH─ proton of the epoxy ring at δ 3.0–3.2 ppm, α-CH$_2$ to C=O at δ 2.2–2.4 ppm, α -CH$_2$ to epoxy group at 1.7–1.9 ppm, β-CH$_2$ to C= O at δ 1.55– 1.7 ppm, β - CH$_2$ to epoxy group at δ 1.4–1.55 ppm, saturated methylene group at δ 1.1–1.4 ppm and terminal − CH$_3$ groups at δ 0.8–1.0 ppm region.

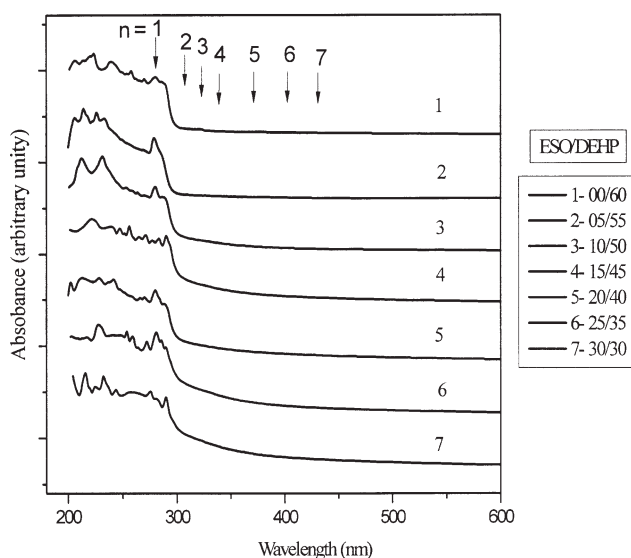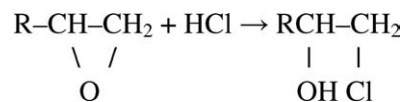$$\text{\textasciitilde CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{\textasciitilde} \rightarrow 2\text{HCl}+\text{\textasciitilde CH=CH-CH}_2\text{-CH=CH}_2\text{\textasciitilde}$$

with Cl substituents on the 2nd and 4th carbons

Scheme 2 PVC dehydrochlorination.

Figure 3 UV-visible spectra of PVC film.

$$R–CH–CH_2 + HCl \rightarrow RCH–CH_2$$
$$\backslash \ / \qquad\qquad | \quad |$$
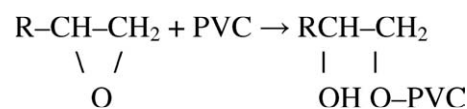$$O \qquad\qquad\qquad OH \ Cl$$

Scheme 3 Reaction of epoxide with HCl.

ionic mechanism under certain conditions. HCl catalyzes the dehydrochlorination, producing polyene sequences with lengths ranging from 6 to 14 conjugated double bonds, to a maximum of 30 units. The reaction can be represented by scheme 2.

The effectiveness of ESO on the thermal degradation of PVC exposed to heat at 100°C for 7 days is shown in Figure 2. This stabilizing effect of ESO is a result of the facile reaction of HCl with epoxy groups to form chlorohydrins, which is thought to reduce the autocatalytic effect of the HCl evolved. Furthermore, the esterification and etherification reactions, which occur with unstable allylic chlorine groups in PVC, provide an explanation for the low-values of the discoloration degrees observed when ESO is used in combination with the Ca/Zn stearates and DEHP.

As shown in Figure 3, where n denotes the number of conjugated double bonds of polyene at the corresponding absorption maximum of the sample in the UV-Visible spectra, the combined effect would reduce the amounts of HCl evolved leading to the formation of short polyene sequences absorbing in the ultraviolet region. Therefore, it was observed that the concentration of the polyenes for plasticized PVC increases rapidly with the decrease of ESO in plasticizer system. However, the increment of polyene with small conjugation number is much greater than that with a larger one. The plasticized PVC demonstrated a decrease in the increment of the concentration of the polyenes with various conjugation numbers (n). A proof for the high stabilizing efficiency is obtained by measuring the extent of discoloration of degraded PVC.[13] The results shown in Figure 3 reveal the lower discoloration of PVC samples was obtained until 15/45 of ESO/DEHP system. It has been reported that the UV–visible absorption wavelength is corresponded to the conjugated chain length of the sample,[14] as can be seen from Table I. Until 25 wt % of ESO in plasticizer system, it exercises a stabilizing effect in presence of DEHP.

Epoxy compounds are well-known as typical nonmetallic stabilizers for PVC. They are generally

For our preliminary study the synmero scale has been used. Figure 2 shows the discoloration degrees of PVC sheets obtained by heat treatment on two rolls milling at 170°C for 10 min and heated in oven at 100°C for 7 days. Good color thermal stability can be seen when ESO is added to DEHP system. In the presence of DEHP, ESO retards the development of discoloration until 45/15 of DEHP/ESO content. After this, a progressive yellow discoloration takes place. During dehydrochlorination, double bond sequences are formed within the PVC polymer chains. The color of the degraded PVC is an indication of the presence of conjugated double bonds from yellow to orange to brown as the number of conjugated double bonds increases. The changes in the discoloration degrees were used as estimates of the relative thermal stability of the plasticized PVC; the higher the discoloration degree, the greater the extent of degradation of the sample. From these results, it is apparent that good stabilization effects of epoxides with metal soaps. This feature was ascribed to the action that the epoxides serve as an acceptor for the excessive cool color producing metal chloride produced from zinc stearate and cadmium stearate to retard the abrupt discoloration of stabilized PVC.[12] The nature of the degradation process occurring with the dehydrochlorination reaction and the catalytic effect exercised by traces of some substance such as H^+, $ZnCl_2$, and $CaCl_3$ suggest an

TABLE I
The Relationship Between UV-Visible Absorption
Wavelength and the Conjugated Chain Length

λ (nm)	287	311	326	342	361	390	419
Length of conjugated diene	3	4	5	6	7	8	9

$$R–CH–CH_2 + PVC \rightarrow RCH–CH_2$$
$$\backslash \ / \qquad\qquad\quad | \quad |$$
$$O \qquad\qquad\qquad OH \ O–PVC$$

Scheme 4 Reaction of epoxide with PVC.

$$2\ -CH_2(-CH=CH-CHCl)_n-CH_2-CH_3 + nCa_3(O_2CR)_2 \rightarrow NO\ reaction$$

Scheme 5 Reaction of allylic chlorine groups in PVC with stabilizer system.

$$2\ -CH_2(-CH=CH-CHCl)_n-CH_2-CH_3 + nZn(OCOR)_2 \rightarrow$$
$$2\ -CH_2-(CH=CH-CH(OCOR))_n-CH_2-CH_3 + nZnCl_2$$

Scheme 6 Reaction of allylic chlorine with stabilizer system.

regarded as secondary stabilizers used to enhance the effectiveness of metal soaps. They act as acceptors for the liberated hydrogen chloride[14,15] and retardants for the appearance of discoloration [as in scheme (3) and (4)]:

From the aforementioned observation and results, it seems reasonable to propose the following mechanism for the stabilization of thermally degraded PVC in the presence of Ca/Zn and ESO. The esterification and reactions, which occur with allylic chlorine groups in PVC, provide an explanation for the synergism observed in the stabilization of PVC containing a combination of an epoxy compound with metal stabilizer. The mechanism of stabilization can be displayed by Schemes (5–7):
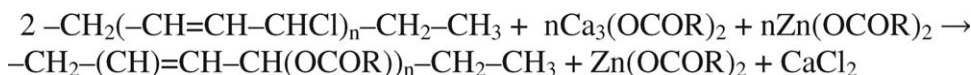
All the samples were subjected to thermogravimetric analysis (TGA), and the data were used to assess the effect of ESO in combination with DEHP on the degradation of PVC sheets. The TGA of the plasticized blends are given in Figure 4. The thermal decomposition temperatures involving two steps of degradation measured from the peaks observed from the first differential of TGA. In the first stage of PVC degradation, the most abundant volatile product is HCl. At low-temperature, molecular dehydrochlorination plays a fundamental role whereas at higher temperature the radical mechanism becomes relevant. HCl formed further catalysis the degradation process releasing more HCl and the formation of polyenes occurs. During the first decomposition stage of this system, the total mass loss was found to be in the range (69.27–76.07%) between 185.23 and 350°C. Thus, this first mass loss represents not only loss of chlorine as HCl, but also loss of plasticizer system or its decomposition products. The mass loss in the second decomposition stage was found to be between (14.05–20.58%) and this occurs at a temperature range of 435–566°C. The loss of HCl makes the allylic chlorine more active in the polymer chain and its unzipping results in polyene linkage, till the conjugated structure is stabilized by resonance. The decomposition temperature in the first step of dehydrochlorination increases with the incorporation of ESO in the plasticizer systems.

Table II summarizes the values of initial degradation temperatures, corresponding to the onset of the plasticizer evaporation and the loss of hydrogen chloride from the PVC molecule. It was concluded that the plasticizer combination affect the thermal stability of the plasticized PVC samples. ESO used in combination with DEHP systems at 15/45 was generally found to be the most effective in retarding the temperature to 205.56°C. ESO tendency to form network structures appears to determine the upper limit of the effective substitution of DEHP by ESO in plasticized PVC formulation.

The plasticized PVC with a single plasticizer has been discussed extensively in the literature. However, its real application, to optimize properties two or more plasticizers are frequently used. The mechanical properties of PVC/(DEHP/ESO) ternary blends were studied. The total plasticizer content is 60 phr in the blend. The variation in the hardness of the plasticized PVC is shown in Figure 5. The hardness Shore A and D values of formulations in presence of ESO in combination with DEHP are lower than that of DEHP alone. Such reduction in hardness with the addition of ESO is attributed to the plasticizing effect of the epoxides. As discussed in above, the incorporation of ESO with DEHP (15/45) appears to produce a synergistic effect.

PVC is a hard and strong material and shows dipole-dipole type attractions as a result of the electrostatic interactions between the chlorine atom of one chain and hydrogen of another. These interactions are weakened by the presence of a plasticizer; such dioctyl phthalate; increasing its flexibility and reducing the viscosity of the molten material; the Young modulus and the T_g.[16] Titow[17] has reported that the level of plasticization of the PVC blends depended on the amount of the plasticizers added. We also investigated the effects of the ESO on the mechanical properties of PVC/(ESO/DEHP) blends. Figure 6 shows the same tensile strength at break with the incorporation of ESO until 20/40 of plasticizer system and it decreases. The formulation with 15/45 of ESO/DEHP (25 wt % of plasticizer system), the elongation at break was the biggest, higher than that of all plasticized samples. The stress at break as

$$2\ -CH_2(-CH=CH-CHCl)_n-CH_2-CH_3 + nCa_3(OCOR)_2 + nZn(OCOR)_2 \rightarrow$$
$$-CH_2-(CH)=CH-CH(OCOR))_n-CH_2-CH_3 + Zn(OCOR)_2 + CaCl_2$$
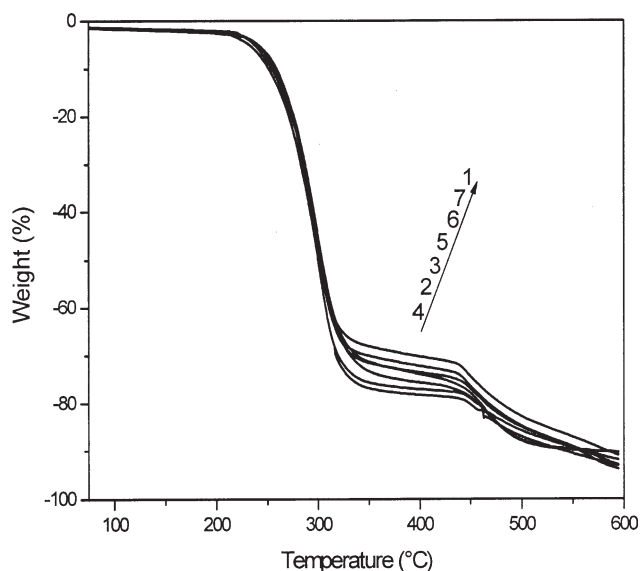
Scheme 7 Mechanism of PVC stabilization with metal stabilizer.

Figure 4 Thermogravimetric curves of samples at 10°C min^{-1} with ESO/DEHP: 1-00/60, 2-05/55, 3-10/50, 4–15/45, 5–20/40, 6–25/35, 7–30/30.

function of the plasticizer content for 20/40, 25/35, and 30/30 samples is shown. These stresses decrease as the plasticizer contents increase. The same behavior the measurement of elongation at break and Young modulus were also observed. This mechanical behavior could be explained by the difference in the T_gs and the viscosity differences of the two plasticizers: ESO presented a lower viscosity, and this enabled its insertion between polymer chains, thereby reducing the inter chain interactions. It can be seen that 15/45 of ESO/DEHP shows good plasticization of PVC compared with all the realized compositions. The dependence of hardness shore A or D is related to the tensile parameters. The variation of hardness with the ESO composition is similar to the Young's modulus and tensile strength at break. The hardness is found to exhibit similar trends as the tensile strength and modulus, and further confirms the observations on modulus.

The dynamical mechanical property of plasticized PVC was measured by DMA and the damping factor (Tang δ) as function of temperature of sheets is shown in Figure 7. The temperature at the maximum point of the loss tangent was taken as the measure of the T_g. An interesting observation from the T_g measurements was that the mixtures of DEHP and ESO and PVC showed a single T_g of formulations investigated, indicating that there is complete miscibility between these additives and PVC over this range. ESO sheets of 0–50 wt % in plasticizer system displayed significantly lower T_g than 78°C, which corresponds to PVC T_g.

These results confirm that addition of both ESO and DEHP causes a small increase in T_g of the PVC compound. A plasticizer behaves similar to a solvent when mixed into a polymer and results in the lowering of the T_g and by this way influences its flexibility. Ziska et al.[18] reported that the appearance of a single T_g was often used as a criterion for blend compatibility. However, besides the compatibility, the interactions between the DEHP and ESO should also be learned in studying the FWHM (full width at half maximum), which is the same until 15/45 in the formulation PVC/(DEHP/ESO) ternary blends.

Table III summarizes the compositions, the α-transition temperature $(T_g)^1$, and the FWHM^2 of all the PVC blends prepared. Incorporating DEHP and /or ESO increases T_g, and ESO/DEHP appears to be a more effective until 15/45, it shifts T_g to ambient temperature (21°C) and comparable value of FMHM to those with lower contents of ESO/DEHP.

Besides the plasticization effect, plasticizers should also be resistant to migration. Migration stability was characterized by the amount of plasticizer migrated out of samples to the liquid phase (extractability) or to the gaseous phase (volatility) under harsh or severe conditions.

Migration behavior was characterized by measuring the weight loss of the specimens under two different test conditions designed to simulate the environments where flexible PVC products are used.

TABLE II
Thermal Decomposition and % Weight Loss for Various Samples Compositions

ESO/DEHP	1st Stage			2nd Stage		
	$T_d{}^a$	$T_{max}{}^b$	% Weight loss	$T_d{}^a$	$T_{max}{}^b$	% Weight loss
00/60	188.50	297	72.26	418.54	460	17.79
05/55	199.09	297	76.07	409.93	465	14.67
10/50	201.14	296	72.65	415.50	455	20.24
15/45	205.56	299	69.27	403.23	457	14.05
20/40	187.54	299	71.22	404.82	450	16.73
25/35	186.26	290	72.61	406.87	445	20.58
30/30	185.23	280	70.20	408.57	446	21.51

^{a} The onset degradation temperature.
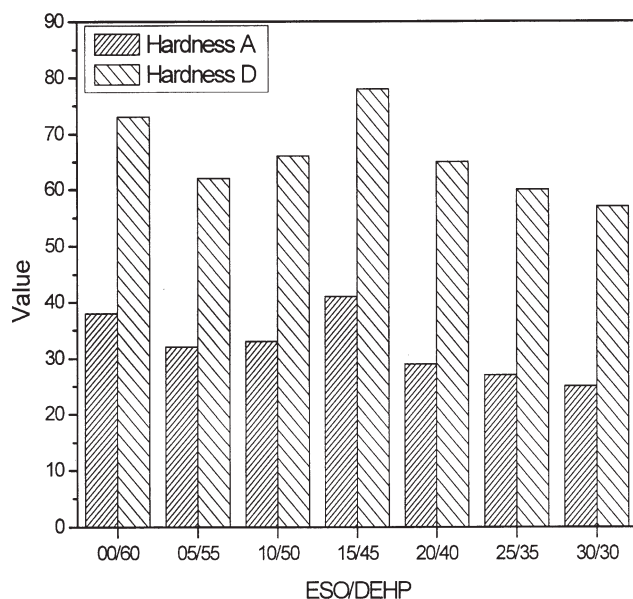^{b} Temperature at maximum weight loss.

Figure 5 Shore Hardness A and D of PVC samples containing various contents of plasticizer system.

The test methods were designed to simulate each representative environment for plasticizer migration into different contacting media. The extraction test simulates the variety of environments where migration may occur to a contacting liquid media of which examples range from food wraps to food packages to bottles to medical blood bags. The volatility test simulates the migration of plasticizer from the flexible PVC product to the atmosphere; for example, to represent plasticizer migration from flexible PVC flooring to air in a closed room at elevated temperature. It is also noted that test methods
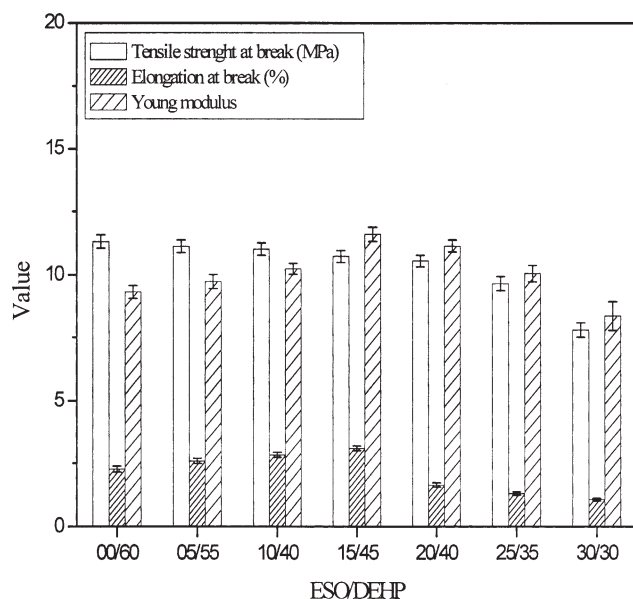

Figure 6 Mechanical properties of PVC sheets containing various contents of plasticizer system.
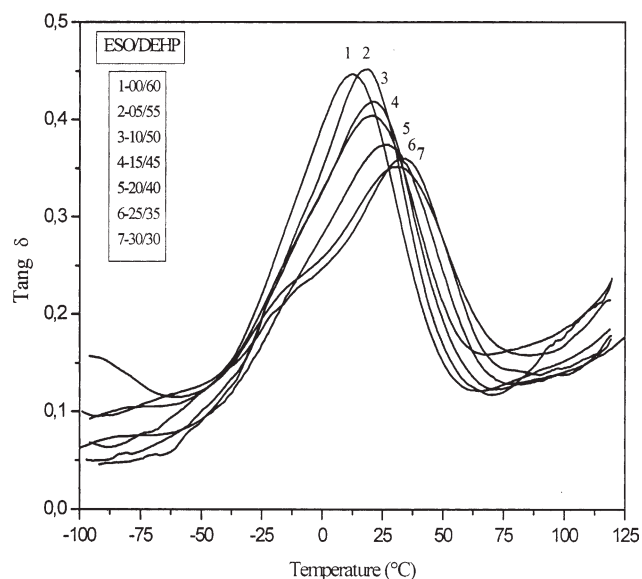
Figure 7 Behavior of glass transition data of the realized formulations.

were modified to accelerate the migration so that the weight loss during the tests would be large enough to contrast the migration in flexible PVC plasticized by ESO/DEHP. In the extraction test, the excess amount of n-hexane with a relatively vigorous mechanical stirring at 40°C accelerated the migration of extractable parts in the blend. In the volatility test, the evaporation of volatile additives was accelerated by putting the specimen sheets in oven at 100°C for 7 days. The extraction and the volatilization of system plasticizers are expressed in terms of the percentage of weight loss after immersion or heating. An increase means that the leaches penetrated the samples, whereas a decrease means that some additives are volatilized. The mass variation data corresponding to the realized formulations with time of contact with solvent or heat are given in Figures 8 and 9, respectively. Figure 8 shows the greatest

TABLE III
Glass Temperature T_g and FWHM of the Realized Formulations from DMA Curves

Plasticizer system content (ESO/DEHP)	T_g (°C)[a]	FMHM (°C)[b]
00/60	12.68	53.96
05/55	18.50	54.15
10/50	21.62	55.61
15/45	21.70	56.90
20/40	26.76	63.40
25/35	33.64	65.87
30/30	31.36	66.74

[a] α-transition temperature is based on the tan δ peak value at 1 Hz measured in DMA.
[b] FWHM (full width at half maximum) here is defined as the breadth (duration of temperature) of the transition peak at half of its maximum peak value.

migration rates occur in the first stages of the process. They then become lower and tend to a minimum as the time increases. It can be seen that the samples from 00/60, 05/55, and 10/50 until 15/45 of ESO/DEHP showed linearly leaching, but the other showed a considerable resistance to leaching, with a maximum weight loss within the duration of the tests less than 8%. This phenomenon arises because when plasticizer migration occurs from flexible PVC in large amounts, the extraction solution slowly fills the vacant locations in the matrix. This means that n-hexane penetrated plasticized PVC, whereas migration of some additives occurred. Further, PVC can shrink and became hard and stiff, so the rate of DEHP migration might decrease with time as a result in all the PVC samples. It may be seen that the amount of DEHP extracted is directly proportional to ESO content. It is expected that DEHP contributes most to the migrated additives. According to current legislation (Directive 90/128/EEC and its amendments; EEC 1990), the overall migration to a foodstuff from food contact plastics must be less than 10 mg of plastic compounds per dm^2 of surface area.

In Figure 9, the volatilization increased at initial period and then gradually to equilibrium. The larger the amount of DEHP, the more intensively loss takes place. The results show low-volatilization from the plasticized samples with those containing low quantities of ESO. This phenomenon can be explained that DEHP permeates into the space of PVC molecular chains when the main two materials, PVC and DEHP are mixed. Intermolecular interaction between the polymer chains decreases with increasing DEHP, and consequently the whole bonding force decreases
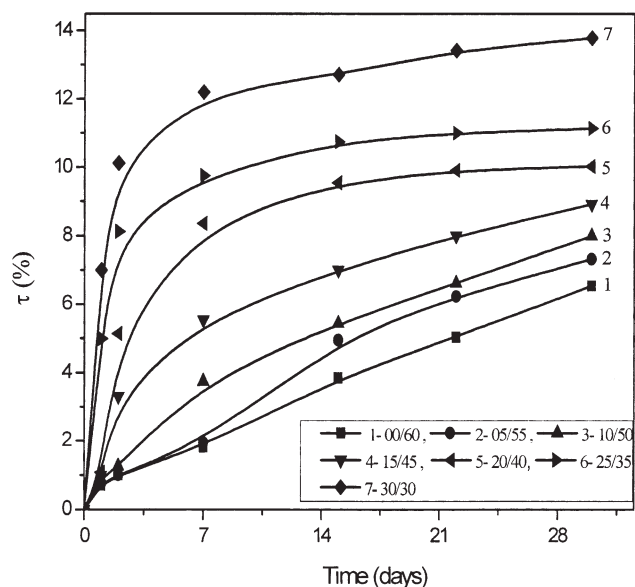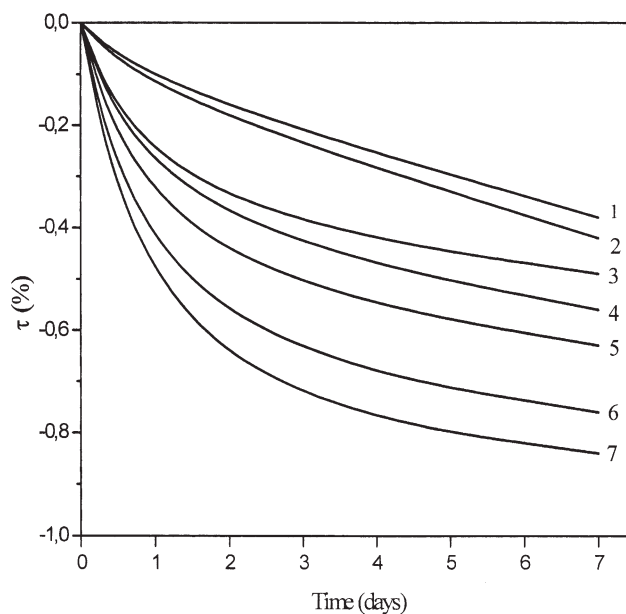

Figure 9 Migration of plasticizer system in oven at 100°C of ESO/DEHP: 1-00/60, 2-05/55, 3–10/50, 4–15/45, 5–20/40, 6–25/35, 7–30/30.

to release more DEHP from PVC matrix. The permanence properties shown by PVC/(DEHP/ESO formulation can be attributed partly to the relatively high molecular weight of ESO and to its thermal behavior (tending to form network structures at elevated temperatures).

Excellent volatility resistance is particularly important in PVC where specifications require minimal losses after air aging. Human exposure to DEHP, estimated to be an average of 1–30 micrograms per kilogram of body weight per day, according to the U.S. National toxicology Program (NTP).

CONCLUSIONS

A clean, facile, and ecologically friendly method for the epoxidation of SO has been developed. ESO is able to be for partial replacement of DEHP at up to 25 wt %, displaying acceptable properties in the areas of thermal and mechanical properties. With the inclusion of epoxy groups, this plasticizer should also have the added advantage of being a heat stabilizer. It was confirmed that ESO is compatible with PVC and has a few plasticizing effects, this was demonstrated both in terms of T_g and in shore hardness.

Plasticizer migration was reduced in proportion to the amount the plasticizer replaced. At moderate (25 wt %) of plasticizer levels of incorporation of ESO moderate improvements in the measured properties of plasticized PVC were observed. The rates of the mass variations increased for both model leachates considered indicating their penetration in or

Figure 8 Migration of plasticizer system in hexane at 40°C.

migration from the plasticized PVC samples. The phenomenon is influenced by the plasticizer concentration, the temperature, the composition, and the nature of the model leachate. At low moderate until 25% levels of incorporation of ESO, moderate improvements in some of the measured properties of the plasticized PVC were observed. ESO tendency to form network structures appears to determine the upper limit of the effective substitution of DEHP by ESO in plasticized PVC. ESO, the derivative of a renewable natural vegetable oil, may be more environmentally friendly than DEHP and other petroleum-based plasticizers.

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