Effects of Epoxidized Sunflower Oil on the Mechanical and Dynamical Analysis of the Plasticized Poly(vinyl chloride)

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ABSTRACT: Epoxidized soybean oil (ESBO), is one of the most commonly used epoxides because of its typical combined roles as a plasticizer and heat stabilizer. In this study, a novel plasticizer of poly(vinyl chloride) (PVC) resins, epoxidized sunflower oil (ESO), was synthesized, and its performance was evaluated. ESO was designed to act as a coplasticizer and a heat stabilizer like ESBO. ESO is used as organic coplasticizer for plasticized PVC containing Ca and Zn stearates as primary stabilizers and stearic acid as lubricant. Di-(2-ethylhexyl) phthalate (DEHP), a conventional plasticizer for PVC, was partially replaced by ESO. Mechanical properties (tensile and shore D hardness) were investigated. The performance of ESO to ESB0 (20 g) for comparison, indicated that ESO could be used as secondary plasticizer for PVC in combination with DEHP. All mechanical and dynamical properties of plasticized PVC sheets varied with the oxirane oxygen of the ESO. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3442–3450, 2008

Key words: PVC; plasticizer; epoxidized sunflower oil; epoxidized soybean oil; mechanical properties; glass transition temperature; DMA

INTRODUCTION

Plasticizers are organic substances added to polymers to improve their flexibility and processability.[1–8] Plasticizer increases the softness, elongation, and low temperature flexibility and decreases the concentration of intermolecular forces and the glass transition temperature (T_g) of polymers.

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 reducing the interactions between the polymer chains and softening the matrix. Plasticizers are required for nearly all polymers used in film coating to reduce the polymers brittleness, improve flow, import flexibility and increase toughness, strength, as well as shear resistance.[7–10] They are classified into primary, secondary, and extenders. Esters, phosphates, and epoxides are the most suitable plasticizers for poly(vinyl chloride) (PVC). Since PVC is polar in nature, mostly ester type plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate are used for its compounds.

Epoxides are well known commercially because of the many important reactions they undergo. Epoxidation of long chain olefins and unsaturated fatty acid derivatives such as soybean oil and other plant oils is carried out on industrial scale. Today, one of the most important epoxidized vegetable oil is epoxidized soybean oil (ESBO),[10–12] its worldwide production is about 200,000 t/year.[13] Fats and oils are renewable resources that can be chemically or enzymatically treated to produce materials that can often act as a replacement for materials derived from petroleum. Fatty epoxides are used directly as plasticizers that are compatible PVC and as stabilizers for PVC resins to improve thermal stability. Because of high reactivity of the oxirane ring, epoxides act as raw materials for a variety of chemicals compounds. Epoxidation is defined as the addition of an oxygen atom across a carbon-carbon double bond to create epoxide (or oxirane) functionality. Epoxidation reactions are typically performed with percarboxylic acids or other peroxy compounds. Epoxidized oil with higher oxirane oxygen value and lower iodine value is considered to be of better quality.[14]

This work is part of a program concerned with the effects of epoxidized sunflower oil (ESO). Sunflower oil is a renewable resource that can be readily epoxidized as described previously.[15,16] ESO has the potential for use as an environmentally friendly reac-

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TABLE I
Formulations Realized with ESO or ESBO

Formulations	1	2	3	4	5	6	7
Poly(vinyl chloride)	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1
Ca/Zn stearates 1/1	1	1	1	1	1	1	1
Di-(2-ethylhexyl) phthalate	30	–	–	30	30	30	30
Epoxidized sunflower oil	–	10	–	10	20	30	–
Epoxidized soybean oil	–	–	10	–	–	–	20

tive material. In this study, mechanical and dynamical properties of PVC/ESO in presence of DEHP are evaluated and compared with the traditional coplasticizer ESBO.

EXPERIMENTAL

Materials

Algerian PVC from ENIP-SKIKDA with K value 65–67 which is a measure of the relative viscosity according to the standard DIN 53-726, Zn stearate from Aldrich (Germany), Ca stearate from Prolabo (France), di-(2-ethylhexyl) phthalate (DEHP) (BASF, Germany) and stearic acid from SOGIS (Italy) were used as received.

Epoxidation process

Sunflower oil with iodine value I(iod) of 130 [g I_2/100 g], from Cévital-Béjaia, Algeria, was used as received. The saponification value, the acid number, and the viscosity were: 193.5 [mg KOH/g], 0.2, and 1476.3 [mPa S] respectively. the epoxidation was carried out according to C=C double bond/acetic acid/hydrogen peroxide molar ration of 1/0.5/1.5, as the acetic acid, which is converted to peracid, is regenerated. The 50% relative excess of hydrogen peroxide versus double bonds was considered as reasonable. Toluene was used as solvent at 50 wt % to sunflower oil. Dried resin and glacial acetic acid were introduced in a 250-mL three-necked flask fitted with a mechanical stirrer, sunflower oil and toluene were then added and the flask was immersed in a thermostated oil-bath. Stirring was started at moderate rate and the temperature was raised up to 55–60°C. Hydrogen peroxide (30%) was added dropwise over a period of 15 min to avoid overheating. After the required reaction time, the oil and aqueous phases were decanted; the organic phase was washed successively with water and 0.1N Na_2CO_3 solution, and rinsed with water. The toluene phase was dried over sodium sulphate and the solvent removed with a rotary evaporator to give the epoxidized oil.

Preparation of PVC sheets

Samples were prepared using the recipes given in Tables I and II. PVC and additives were mixed in a roll mill at 160°C.

The sheets were compression molded to make plaques, which were required for some of the tests. The operating temperature was 160°C for 12 min with hydraulic pressure of 20 tons.

Measurements

Discoloration

The evolution of discoloration was measured using ten degrees color scale (Synmero) as described by Ockay et al.[17]

UV–visible analysis

UV–visible spectra of purified samples of PVC in distilled tetrahydrofuran (THF) (C = 2 g/L) were obtained by using a UNICO-Logiciel vision 32-v1-10 spectrophotometer. The samples were purified by two cycle of dissolution in THF, precipitation (meth–

TABLE II
Formulations Realized with ESO Containing Various Oxirane Oxygen Levels

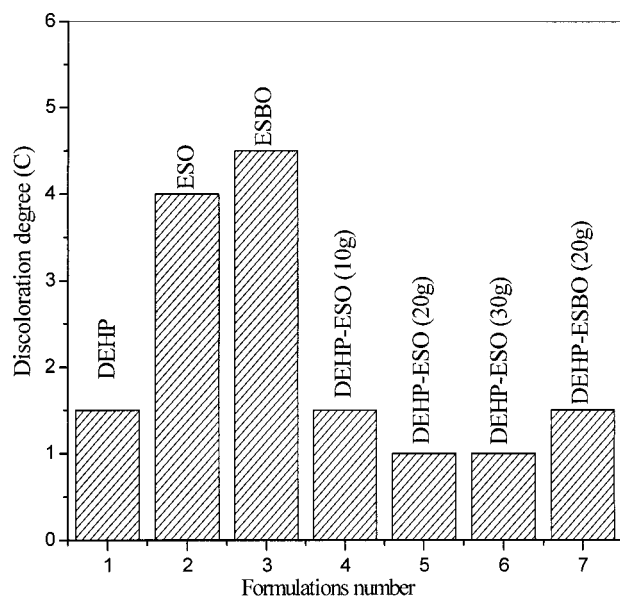| Formulations	8	9	10	11	12	13	14
Polyvinyl chloride	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1
Ca/Zn stearates	1	1	1	1	1	1	1
Di-(2-ethylhexyl) phtalate	30	30	30	30	30	30	30
Epoxidized sunflower oil	20	20	20	20	20	20	20
Oxirane Oxygen (O.O %)	(0)	(1)	(2)	(3)	(4)	(5)	(6)

Figure 1 Discoloration of PVC sheets with various weight plasticizers system.

anol), and filtration. The recuperated powder was dried under vacuum at room temperature.

Hardness

The shore D hardness test was carried out according to ISO 7619 using a Zwick 7206 Hardness Tester. Sheets of 6-mm thickness were used for hardness measurements. Specimens of 7-mm thickness were produced by compression molding. Ten measurements were made on each sample type.

Tensile

The mechanical properties of the control PVC (PVC containing DEHP) alone as well as other plasticized samples were determined according to ASTM-D412-8O test method. The stress–strain curves in tensile mode were obtained by means of a universal testing machine (Model instron 1011) at a strain rate of 10 mm/min.

Dynamical mechanical analysis

All experimental data were collected on a TA instruments DMA 2980 machine, using the tension film clamping arrangement. Specimens were excited using a 20-μm dynamic displacement, and a small preload (0.2 N) to insure that the specimens were always in tension. The measurements of the complex Young's modulus were made over a temperature range from −50 to 130°C, in 2°C intervals, at the following frequencies: 1, 3, 5, 10, 15, 20, 35, and 50 Hz. The temperature was allowed to come to equilibrium and held constant while measurements were made at each frequency.

RESULTS AND DISCUSSION

Evolution of discoloration

Plasticizer performance data were obtained on milled sheets prepared on a laboratory roll mill. For our preliminary study the Synmero scale has been used. Figure 1 shows the discoloration curves of PVC sheets containing various plasticizers systems. In the absence of DEHP, ESO has no effect on the retardation of the development of discoloration.

The ESO in presence of DEHP uniformly showed excellent effect on the initial coloration. This efficiency generally was equal to or better than ESB0 alone or combined with DEHP.

The coloration decreases with increasing the weight of ESO in presence of DEHP. ESO exhibits a relatively better effect than ESBO on the development of discoloration.

Figure 2 presents the influence of the levels of the oxirane oxygen in the ESO in presence of DEHP. The increase of oxirane oxygen of ESO decreases the discoloration degree of PVC sheets. The epoxy group of the plasticizer is excellent hydrochloric acid scavenger; hydrochloric acid absorption occurs readily.[18–20]

The formation of polyene sequences was investigated by UV–visible spectroscopy. The influence of the weight of the epoxidized oil and the amount of oxirane oxygen in the ESO were considered. The inherent stabilizing action is indicated in the accompanying Figures 3 and 4 illustrating the performances of the epoxidized at different weights in purified milled sheet formulations.
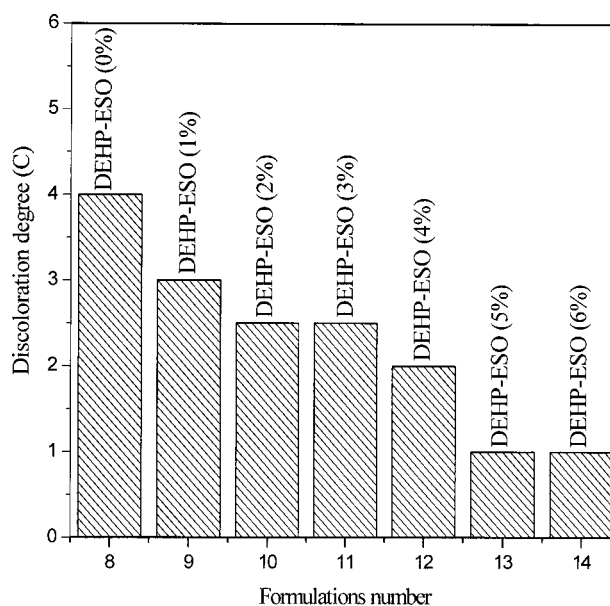

Figure 2 Discoloration of PVC sheets plasticized with epoxidized sunflower oil containing various levels of epoxidation.

1- DEHP
2- ESO
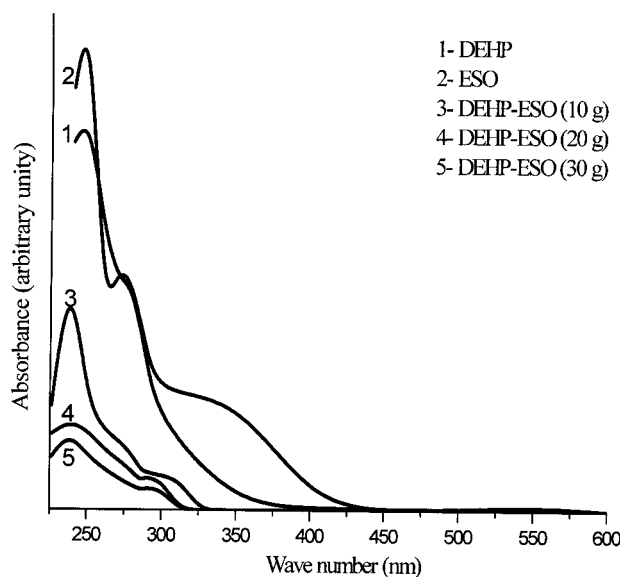3- DEHP-ESO (10 g)
4- DEHP-ESO (20 g)
5- DEHP-ESO (30 g)

Figure 3 UV–visible spectra of purified PVC sheets with various weights of epoxidized sunflower oil.

The stabilizing action of the epoxy fatty acid is attributed to the presence of the epoxy group in the plasticizer chain. Modern theory holds that the degradation of polyvinyl chloride polymer under heat or light excitation is a complex series of reactions proceeding initially through a dehydrochlorination and leading to polyene structures (Scheme 2).[21,22]

Color formation accompanies the progressive appearance of chromophoric carbon-carbon bonds. In turn, the double bonds of the degraded polymer are potentially the site of further oxidative attack leading to color contributing carbonyl groups. The initial degradation appears to be a random splitting
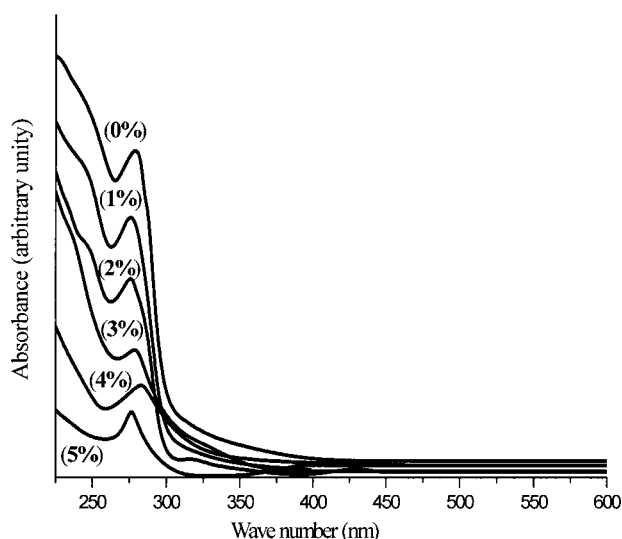
out of hydrochloric acid from the polymer; the released hydrochloric acid in turn catalyzing the progressive further polymer breakdown.

Stabilization systems are dependent upon addition of a stabilizer believed to function by removing released hydrochloric acid, reacting with the double bonds of the formed polyene inhibiting oxidation of the polyene or inhibiting free radical transfer.

The result is retarded polymer degradation and diminished color formation. Where processing conditions are mild, epoxy fatty acid plasticizers may be used. With the addition of metallic stabilizers, greatly enhanced stabilizing action can be achieved, frequently with use of less than conventional stabilizer amounts. Various metallic stabilizers, notably those based on calcium and zinc, are believed to behave synergistically with epoxy compounds as far as stabilizer properties are concerned.
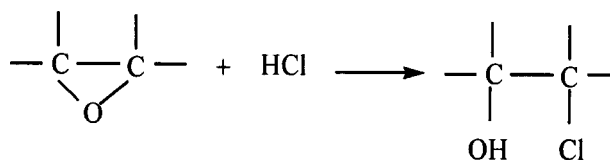
The oxirane ring is a well known acid acceptor in PVC. HCl from initial degradation is scavenged by the epoxide, converting the epoxy group to a chlorohydrin (as seen in Scheme 1). It has also been suggested that the epoxy ring might act as a polyene blocker, opening by reaction at a labile hydrogen site in the PVC to form an ether linkage with the chlorinated epoxy (Scheme 3).
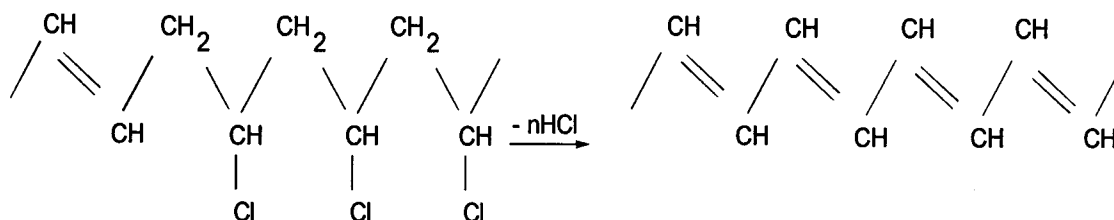
Mechanical properties

The most important measuring results namely the tensile strength, the stress, elongation at break, Young's modulus, and shore D hardness of the plasticized PVC films are shown in Table III. The tensile strength decreases gradually with the content of ESO, whereas the % elongation at break increases. In presence of DEHP, the comparison of ESO to ESBO at the chose weight 20 g shows that ESO presents best properties than ESBO.

It can be seen that the mechanical properties are affected by the weight of ESO. The plasticizing efficiency can be evaluated taking into account the flexibility of sheets. The values of tensile strength, elongation at break, and shore D hardness show the highest flexibility trend. The plasticizing effect of ESO was higher because of its lower molecular and its higher compatibility with PVC.

Formulations 4, 5, and 6 which contain 10, 20, and 30 parts of ESO confirm the effect of ESO as secondary plasticizer: It is understood that the plasticizing

Figure 4 UV–visible spectra of purified PVC sheets plasticized with epoxidized sunflower oil containing various levels of epoxidation (0–5% O.O).

Scheme 1 Reaction of oxygen oxirane and HCl.

Scheme 2 Polyene structures of degraded PVC.

efficiency of ESO depends on the weight of particular components in the molecule. This is a correlation between the values of mechanical properties: higher shore D hardness and higher tensile strength values correspond in general to lower elongation at break.

The increase in tensile strength and decrease in % elongation at break with ESO (20 g of weight) is attributed to the level of O.O, which increases the cohesive energy density (intensity of intermolecular attractions), such that with a higher polarity, materials tend to hold themselves together more tightly. As a result the chain mobility and thus the flexibility of the compound are reduced, although the increase strength and decrease in % elongation at break with ESO may also be attributed to its high molecular weight and viscosity.

Our results have demonstrated that ESO could indeed be used as a plasticizer for PVC. There are several advantages of using this epoxidized oil as plasticizer. Firstly, sunflower oil is relatively inexpensive commodity and the epoxidation is relatively simple process. Secondly, the epoxidized oil impart a good heat stabilization effect; PVC plasticized with ESO was found to exhibit better thermal stability than PVC plasticized with DEHP. Thirdly, as this oil was derived from the natural triglycerides, it is likely to be more suitable for application in food grade PVC products.

Dynamical mechanical analysis

The control sample contains only DEHP (30 g). When incorporating the ESO or ESBO in PVC, the influences of this secondary plasticizers content on the plasticization effects of DEHP in the PVC were evaluated by DMA measurements. Figure 5(a–c), show the effect of plasticized PVC sheets on loss tangent (tan d) and storage modulus as a function of test temperature for DEHP, ESO, and ESBO, respectively. Multi-frequency data of 1, 3, 5, 10, 15, 20, 35, and 50 Hz were collected during the temperature scan. The damping property of plasticized PVC increases with an increase in frequency. An increase in frequency shifts the tan d and the storage modulus curves to higher temperatures. The nature of the plasticizer changes the shape of the curves. It can be seen that tan d showed a peak around temperatures between 46.3 and 56.9, this being know as a transition region. In this case, samples containing ESO or ESBO alone showed comparable T_g. The similar storage modulus curves of ESO and ESBO remained constant at lower temperatures, but showed a sharp drop followed by a plateau as the temperature increased. This region is the transition region where the polymer changes from glassy state to rubbery state. Inspection of the dynamic modulus spectra shows the plasticizing action of ESO.

The principal peak temperature, which is obvious in the tang d results, is distinctly assigned to the glass transition temperature of the corresponding formulation. For the series with varying the weight of ESO in presence of DEHP [see Fig. 6 (a–d)] and in comparison to ESBO, it is noted that T_g systematically decreases with epoxy addition. As the ESO content was increased, the maximum loss tangent (tan d_{max}) shifted to lower temperatures and the peak height reduced to low with diminution of frequency. The amount of shift on changing the frequency depends on the tang d and also on its energy of activation.[23]
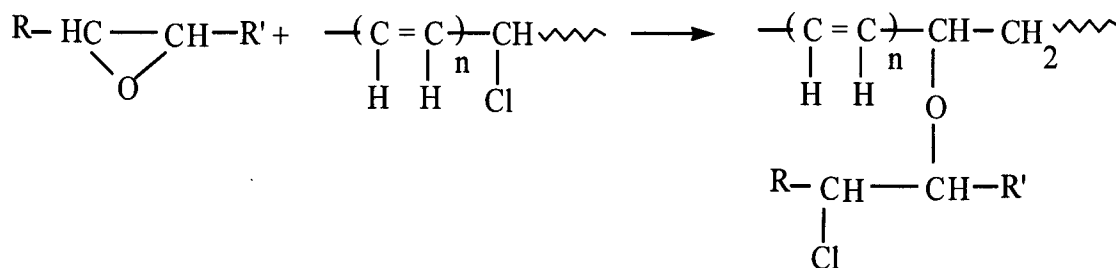
Scheme 3 Reaction of PVC with the epoxidized compound.

TABLE III
Mechanical Properties of Compounds

Formulation number	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)	Shore D hardness
1	32	136	475	4
2	59	3	3555	57
3	48	2	1900	56
4	32	163	111	9
5	28	176	61	8
6	25	182	36	7
7	27	163	26	9
8	19	82	262	22
9	35	135	64	21
10	34	147	61	20
11	32	155	50	19
12	29	169	44	16
13	25	172	41	8
14	24	178	39	6

The loss tangent spectra are typical of a miscible system by showing one T_g and there is only a moderate broadening of the main T_g relaxation. This suggests that the blends PVC–DEHP–ESO are homogeneous. The DMA of PVC-DOP shows a lower tan d; and a broad peak; or a lower homogeneity. The incorporation of oxirane in sunflower oil reduces the degradation of PVC and reduces it progressively with the increase of oxygen oxirane.

It is accepted that the higher the tan d_{max} the greater the mechanical loss; these losses are related to high energy input required for the motion of the molecular chains of the polymer as the transition is being approached. The results also suggested that increasing the weight of ESO content caused an increase of elastic behavior (reduced tan d_{max}).

In the tan d presentation, a narrow relaxation peak dominated over the entire temperature of measurement from −50°C to about 130°C. Peak temperatures measured tan d at various frequencies is tabulated in Table IV. As expected, the higher content plasticizer samples had lower glass transition temperatures. In other words, the plasticization effect of ESO on the PVC increases with increasing ESO content.

Finally, another interesting observation relating to the T_g behavior of ESO is that the increase of oxirane
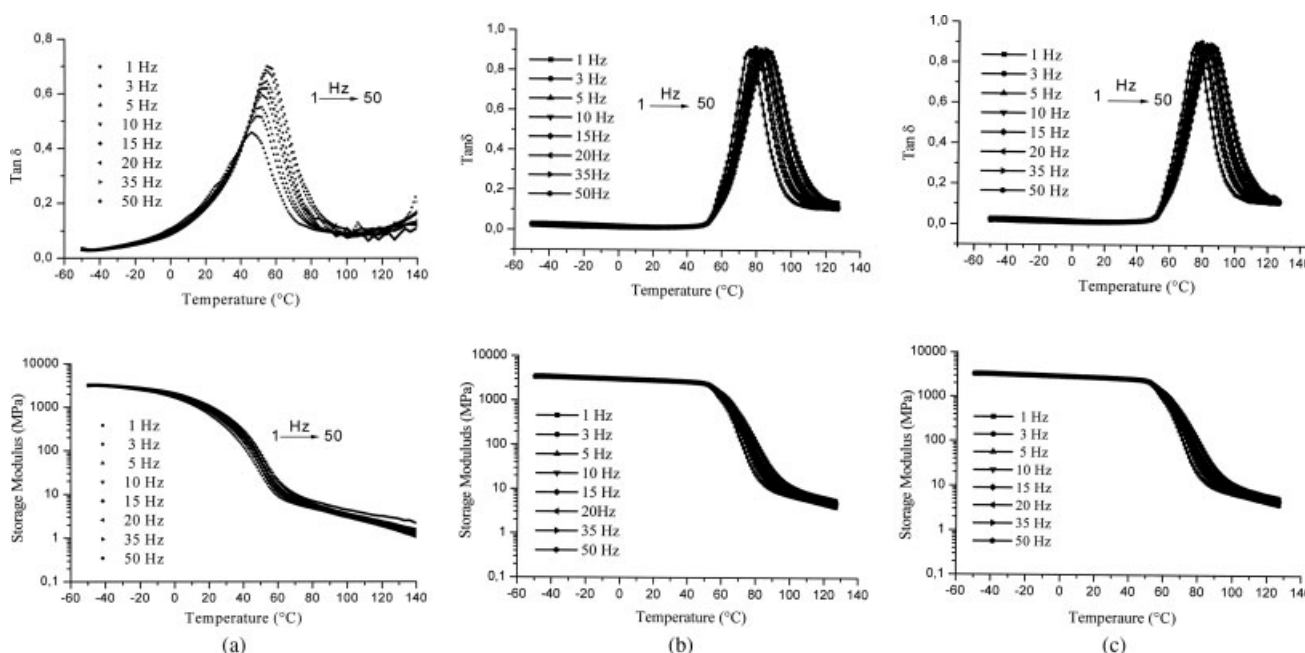

Figure 5 Loss tangent curves and storage modulus as function of temperature for plasticized PVC with: (a) DEHP, (b) ESO, and (c) ESBO.
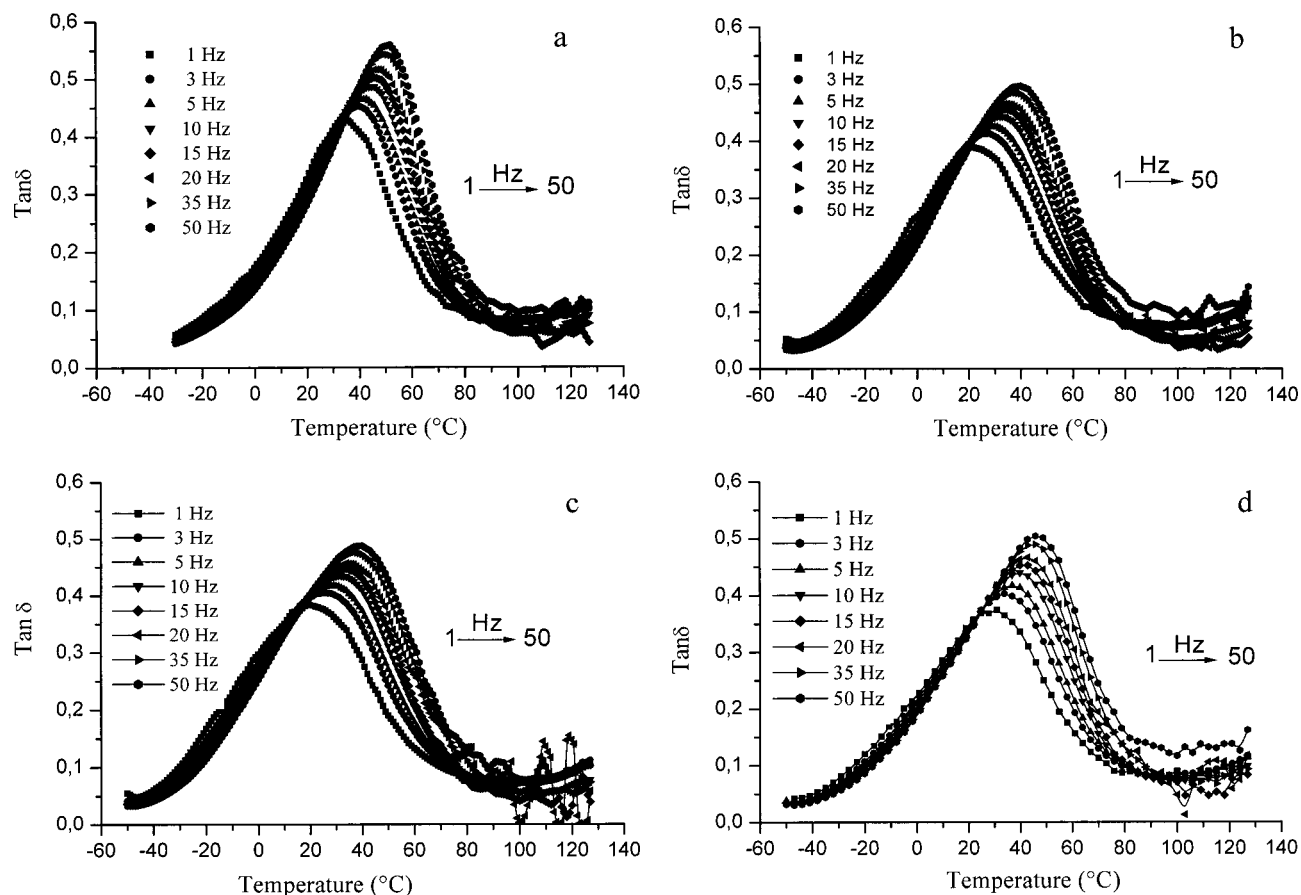
Figure 6 Loss tangent curves as function of temperature for (a) DEHP-ESO 10 g, (b) DEHP-ESO 20 g, (c) DEHP-ESO 30 g, and (d) DEHP-ESBO 20 g.

oxygen decreases the T_g of PVC sheets. Substantial physical property changes occur with increasing level of epoxidation; thus as the level of epoxidation goes up the glass transition temperature (T_g) decreases.

Figure 7 also shows that the epoxidation levels of ESO in combination of DEHP are divided into two groups: with less (sample 8, 9, and 10) and those with more than 3% O.O (sample 11, 12, 13, and 14); this also reflected on tan d_{max} versus their optimum composition behavior and its affinities. In the first

group from 0 to 2% O.O T_g decreases slowly, but in the second group from 3 to 6% O.O T_g decreased rapidly. Increase in frequency of the testing displaced the T_g value to higher temperatures.

It was interesting to plot the value of tan d_{max} to verify the effect of frequency on the change in activation enthalpy by using Arrhenius law. From the frequency dependence of the T_g peak, the values of activation enthalpy for the plasticized samples are calculated, showing the thermally activated character of this process (Fig. 8) and given in Table V, where

TABLE IV
Glass Transition Temperatures (T_g) for Various Plasticized PVC Sheets

Notation (Formulation)	Frequencies (Hz)							
	1	3	5	10	15	20	35	50
F1 (DEHP 30g)	46.3	50.3	51.6	52.3	53.6	54.5	55.1	56.9
F2 (ESO 10g)	75.6	78.5	79.8	81.5	82.6	83.5	85.1	86.2
F3 (ESBO 10g)	75.9	78.1	79.1	80.8	82.4	83.1	84.8	85.8
F4 (DEHP 30-ESO10g)	34.2	39.8	41.5	44.9	46.1	47.5	49.7	51.3
F5 (DEHP30-ESO20g)	21.8	27.5	29.2	32.5	34.0	35.2	38.1	39.9
F6 (DEHP30-ESO30g)	19.6	25.4	28.5	31.7	33.6	34.4	37.4	38.8
F7 (DEHP30-ESBO20g)	30.2	34.2	36.8	39.6	41.5	42.7	45.0	46.5

Values in the table indicate glass transition temperature T_g (°C).
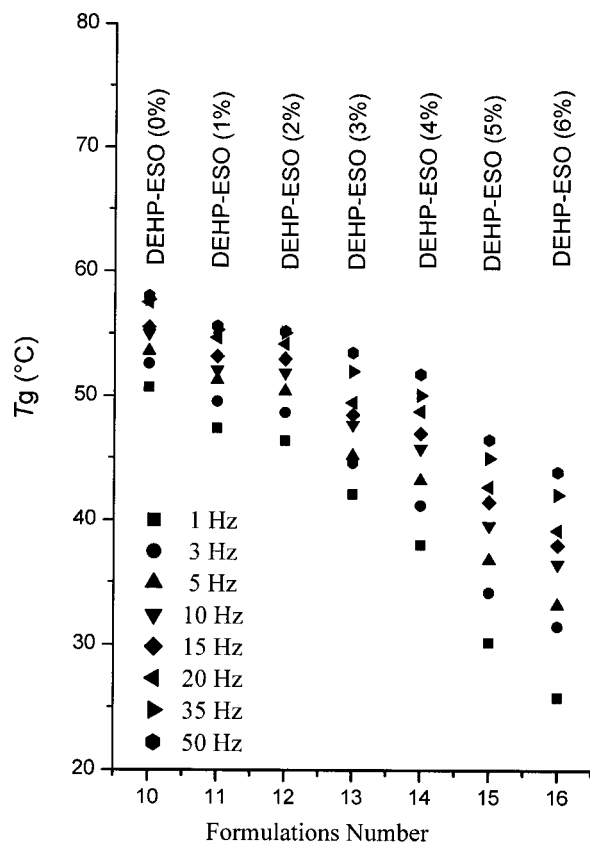
Figure 7 Glass transition temperatures for plasticized PVC sheets with various oxirane oxygen of ESO.

ΔH is the activation enthalpy for the relaxation process. It appears that there is a monotonic dependence of the activation enthalpy on the measured T_g. This dependence could have arisen from the complete miscibility between the dominant amorphous phase of PVC and the DEHP-ESO. The points corre-
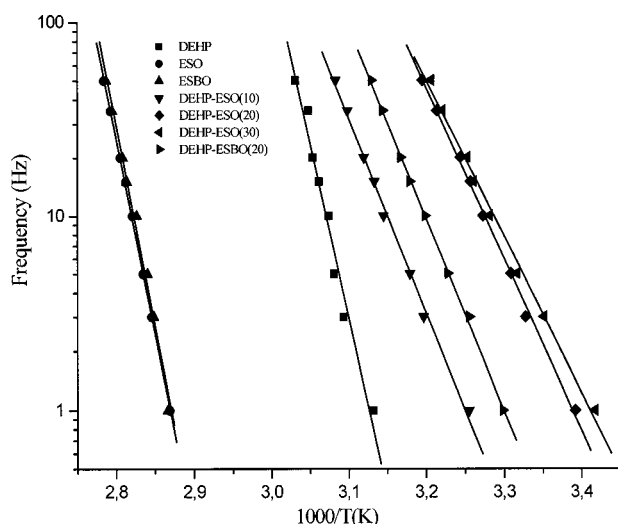

Figure 8 Activation enthalpy for different system plasticizers of PVC sheets.

Notation (Formulation)	Activation enthalpy $\Delta H/\text{kcal mol}^{-1}$
F1 (DEHP 30g)	18.1
F2 (ESO 10g)	20.2
F3 (ESBO 10g)	21.2
F4 (DEHP 30-ESO10g)	10.1
F5 (DEHP30-ESO20g)	8.9
F6 (DEHP30-ESO30g)	8.1
F7 (DEHP30-ESBO20g)	9.9

sponding to the plasticized PVC samples are shifted toward lower value of activation enthalpy.

Epoxidation of sunflower oil is essential, as it improved compatibility as well as thermal stability. This study demonstrates some of potential industrial applications of sunflower oil, many of which have yet to be fully exploited.

CONCLUSIONS

Existing results give evidence that the presence of ESO in PVC mixtures brings about an appreciable decrease in degradation of PVC and contributes to preservation of the color of the mixture. The study shows that ESO could be used as a secondary plasticizer for PVC. ESO is suitable above all for its cooperative effects. It can be regarded as stabilizer as well as good plasticizer.

The physical interaction or solubility of ESO seemed to be more likely reason for such changes in the properties of flexible PVC. When the plasticizer content was increased, there was a decrease in tensile strength and shore D hardness.

The presence of ESO in formulation with DEHP greatly enhances the thermal and mechanical characteristics. Dynamical mechanical analysis reveals that ESO can function as coplasticizer for PVC-DEHP systems by the lower T_g values obtained for various oxirane oxygen.

The plasticizing effect of ESO was higher than that of ESBO because of the lower molecular weight of ESO and its higher compatibility with PVC.

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