

# Thermal and mechanical properties of bio-based plasticizers mixtures on poly (vinyl chloride)

Boussaha Bouchoul<sup>1\*</sup>, Mohamed Tahar Benaniba<sup>1</sup> and Valérie Massardier<sup>2</sup>

<sup>1</sup>Laboratoire des Matériaux Polymérique MultiPhasiques – LMPMP, Département de Génie des Procédés, Faculté de Technologie, Université Sétif 1, Algérie

<sup>2</sup>Laboratoire Ingénierie des Matériaux Polymères UMR 5223, Centre National de la Recherche Scientifique – CNRS, Institut National des Sciences Appliquées de Lyon – INSA, Lyon, Villeurbanne, France

\*B\_Bouchoul@yahoo.com

## Abstract

The use of mixtures of nontoxic and biodegradable plasticizers coming from natural resources is a good way to replace conventional phthalates plasticizers. In this study, two secondary plasticizers of epoxidized sunflower oil (ESO) and epoxidized sunflower oil methyl ester (ESOME) were synthesized and have been used with two commercially available biobased plasticizers; isosorbide diesters (ISB) and acetyl tributyl citrate (ATBC) in order to produce flexible PVC. Different mixtures of these plasticizers have been introduced in PVC formulations. Thermal, mechanical and morphological properties have been studied by using discoloration, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), tensile - strain and scanning electron microscopy (SEM). Studies have shown that PVC plasticization and stabilization were improved by addition of plasticizers blends containing ISB, ATBC, ESO and ESOME. An increase in the content of ESO or ESOME improved thermal and mechanical properties, whereas ESOME/ATBC formulations exhibited the best properties.

**Keywords:** PVC, epoxidized sunflower oil, epoxidized sunflower oil methyl ester, isosorbide diesters, acetyl tributyl citrate.

## 1. Introduction

Poly (vinyl chloride) (PVC) is very present in daily living applications due to its diverse properties and low cost<sup>[1,2]</sup>. Its properties depend on the amount of different kinds of additives such as plasticizers<sup>[3]</sup>. The plasticizer is a very important additive of PVC; it can improve the flexibility of PVC without changing its chemical properties<sup>[3-6]</sup>. Phthalates are the most commonly used plasticizers in PVC with applications in food packaging, medical devices, children's toys, building materials, and other common products<sup>[3]</sup>. Unfortunately, phthalates contaminate indoor environments, human food and are environmental contaminants. It has been reported by Bhakti et al.<sup>[3]</sup> that several phthalates and especially diethyl hexyl phthalate (DEHP) also known as di-octyl phthalate (DOP) are suspected of having carcinogenic and toxic effects.

Recently, several alternatives exist to substitute DEHP in PVC applications<sup>[3]</sup>. Nowadays, there is an increasing interest in the use of nature based plasticizers for PVC<sup>[7,8]</sup>. Some studies have been done on the use of epoxidized sunflower oil (ESO) as secondary plasticizer to partially replace di-2-ethylhexyl phthalate (DEHP) in PVC formulations<sup>[9,10]</sup>. The compatibility of plasticizers with PVC also needs to be considered<sup>[11]</sup>. Solubility parameters are often used to predict PVC/plasticizer interactions. Decrease in the glass transition temperature ( $T_g$ ) of PVC can also be studied to assess plasticization efficiency<sup>[12]</sup>.

Epoxidized sunflower oil (ESO) and epoxidized sunflower oil methyl esters (ESOME) were synthesized and then characterized by oxirane index titration and FTIR spectroscopy. The aim of the work reported here is to investigate the use

of these new products as secondary plasticizers, mixed with isosorbide diesters (ISB) and acetyl tributyl citrate (ATBC) to plasticize PVC with 60 parts of plasticizers mixtures. The plasticization of PVC with ISB, as well as with its mixtures containing ESO and DEHP, has been studied in our previous work<sup>[13]</sup>. Although ATBC and ISB have been studied as individual plasticizers for this polymer<sup>[13,14]</sup>, ATBC, ISB and their mixtures with ESO or ESOME in PVC is the axis of the present research to evaluate thermal, mechanical and morphology characteristics of plasticized PVC. Discoloration degree of sheets, thermogravimetry analysis (TGA), dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), mechanical properties and scanning electron microscopy (SEM) were used to investigate the properties of our PVC plasticized with ATBC, ISB and their blends with ESO or ESOME.

## 2. Materials and Methods

### 2.1 Materials

PVC suspension grade resin (SE 950, K= 65.7-67.1), was kindly supplied by Shintech (Houston, USA). Plasticizers used were as follows: acetyl tributyl citrate (ATBC) (Sigma Aldrich, USA), isosorbide diesters (ISB) (ID47, Roquette Frères, France), sunflower oil (SO) with an iodine value index,  $I_{\text{iod}}$ , of 130g I<sub>2</sub>/100g (Cevital Bejaia, Algeria), epoxidized sunflower oil (ESO) with 6.1% of oxirane oxygen (conversion = 98.2%, yield = 80.5%) and epoxidized sunflower oil methyl ester (ESOME), were prepared in our

laboratory. Ca/Zn stearates and stearic acid (SA) were used as thermal stabilizer and lubricant, respectively.

## 2.2 Methods

### 2.2.1 Epoxidation of sunflower oil

Sunflower oil (SO) and formic acid were combined in a 250 mL three neck flask equipped with stirrer, reflux condenser and thermocouple. The three neck flask was immersed in a heating mantle. Reaction occurred during mixing of the feed components and the reaction temperature was controlled at 55°C. To start the epoxidation, hydrogen peroxide solution (30%) was then added dropwise into the mixture for the first 30 minutes of reaction. The mole ratio of carbon double bonds to hydrogen peroxide (C=C: H<sub>2</sub>O<sub>2</sub>) was 1: 1.5. After feeding H<sub>2</sub>O<sub>2</sub> was completed, the reaction continued by mixing at a stirring speed of 700 rpm and controlling the temperature at 55°C for a further two hours. After that, the product of reaction was next cooled and decanted for the separation of the organic soluble compounds (epoxidized oil) from the water soluble phase. The epoxidized sunflower oil (ESO) was then washed with warm water to remove residual contaminants. Diethyl ether was used to enhance the water separation<sup>[15]</sup>. The washed organic layer was also dried with centrifugation to remove water traces in the epoxidized oil. The epoxy functionality was determined using AOCs Cd 9-57 method<sup>[16]</sup>.

### 2.2.2 Transesterification of epoxidized sunflower oil

Reactions were performed in a 250 mL flat bottom glass vessel. Epoxidized sunflower oil was introduced to the glass vessel along with a magnetic stir bar. Sodium methoxide catalyst was dissolved in methanol and then added to the epoxidized sunflower oil in the reactor<sup>[17]</sup>. This mixture was heated to 50°C on a hot plate and magnetically stirred at 700 rpm. The reaction was stopped after 2 hours and the reaction mixture was transferred to a separatory funnel to recover the products. Then, the oxirane index is measured to confirm the no opening of oxirane cycles.

### 2.2.3 Fourier transform infrared spectroscopy (FTIR)

The samples were identified using Fourier transform infrared spectroscopy with a 680 Nicolet thermo spectrometer (Thermo Scientific, USA), employing an Attenuated Total Reflection (ATR) accessory, equipped with a diamond crystal cell, angle 45°. The spectra were acquired in the range 4000-500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and the signal

was averaged over 32 scans. Spectra were obtained by direct measurement.

### 2.2.4 Preparation of PVC sheets

The plasticized PVC sheets were prepared using PVC, ISB, ATBC, ESO and ESOME. Various combinations (on weight basis) were prepared and used as plasticizing mixtures. Four series of blends were prepared: PVC/(ISB/ESO), PVC/(ISB/ESOME), PVC/(ATBC/ESO), PVC/(ATBC/ESOME) and one formulation of PVC/DEHP as reference. In each case, 60 parts of this mixture was mixed with 100 parts of PVC. The different combinations used for the preparation of PVC sheets are displayed in Table 1.

Samples prepared with different plasticizer combinations were further mixed for 10 minutes by using a two roll mill at a temperature of 160°C to obtain a homogeneous blend.

### 2.2.5 Discoloration sheets by static heat

Circular test pieces (19 mm diameter) were placed in a circulating air oven maintained at 177± 2°C. Test pieces were removed at intervals of 5, 10, 15, 20, 30, 45, 60, 80, 100, 130, 160 and 200 minutes. The color changes with the heating time were observed and measured with color Synmero scale as described by Ocskay et al.<sup>[18]</sup>.

### 2.2.6 Thermogravimetry analysis (TGA)

Thermal degradation studies were conducted using a thermogravimetry analyzer TGA (Q500 TA Instruments, USA). All the samples were evaluated from ambient to 500°C under nitrogen flow (40 mL/min) at 10°C/min heating rate.

### 2.2.7 Differential scanning calorimetry (DSC)

Glass transition temperature (T<sub>g</sub>) was determined by differential scanning calorimetry using a DSC Q10 (TA Instruments, USA) calibrated with indium. Samples of about 8 mg were conditioned in aluminum pans, equilibrated at 25°C and held isothermally for 1 min. Then, they were heated to 220°C at 20°C/min and held isothermally for 3 min at 220°C to eliminate previous thermal history. The samples were then cooled to -60°C and held isothermally for 3 min and finally heated to 220°C at a constant rate of 10°C/min.

### 2.2.8 Dynamic mechanical thermal analysis (DMTA)

All tests were conducted with RSA Rheometrics. The analyses were carried out on specimens measuring 30x7x0.5 mm<sup>3</sup> in tensile mode with a temperature ranging from -60°C to 80°C at a 3°C/min heating rate with frequency

**Table 1.** Compositions of our plasticized formulations.

Materials (phr)	Formulation number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100	100
SA	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Ca/Zn	2	2	2	2	2	2	2	2	2	2	2	2	2	2
ISB	60	50	40	30	-	-	-	-	50	40	30	-	-	-
ATBC	-	-	-	-	60	50	40	30	-	-	-	50	40	30
ESO	-	10	20	30	-	10	20	30	-	-	-	-	-	-
ESOME	-	-	-	-	-	-	-	-	10	20	30	10	20	30

of 1, 3, 5 or 10 Hz.  $T_g$  was taken at the peak in the  $\tan \delta$  curve accompanied by a step reduction in the storage modulus.

### 2.2.9 Mechanical properties

Test specimens were cut according to NF T 51-034 H1. The Young's modulus, tensile strength and elongation at break were determined at room temperature with a universal dynamometer (Instron, ref. 33R4469, USA) at constant rate of 50 mm/min by using a 0.5 kN sensor.

### 2.2.10 Scanning electron microscopy (SEM)

Morphological studies were conducted using a scanning electron microscope JEOL (model JFM-6360 LV). Specimens were sputter-coated with gold to a thickness of 10 nm before surface characterization to prevent charging. The SEM was equipped with a lanthanum hexaboride (LaB6) crystal as electron emitter source. An accelerating voltage of 13 kV was used to collect the SEM images.

## 3. Results and Discussion

### 3.1 Epoxidation of sunflower oil (ESO)

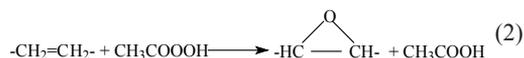
There are two main reactions involved in the epoxidation reaction as mentioned above. During the first stage, peroxy acid is formed from the reaction of formic acid and hydrogen peroxide while, in a second stage, epoxidized sunflower oil is produced from the reaction between peracid and double bonds in the sunflower oil<sup>[19]</sup>.

The following reaction scheme considers hydrogen peroxide as oxygen donor and acetic acid as oxygen carrier<sup>[20]</sup>:

Step 1: Formation of Peroxy formic acid

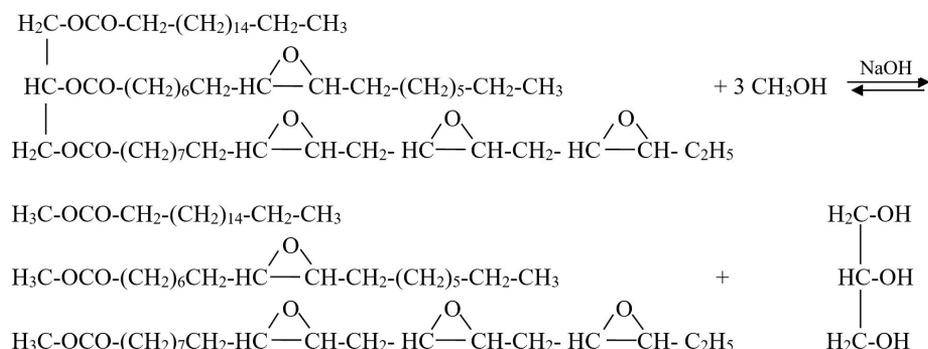


Step 2: Epoxidation Reaction



### 3.2 Transesterification of epoxidized sunflower oil

In the transesterification, ESO reacts with methanol in the presence of NaOH, and produces a mixture of epoxidized fatty acids alkyl esters and glycerol (Scheme 1).



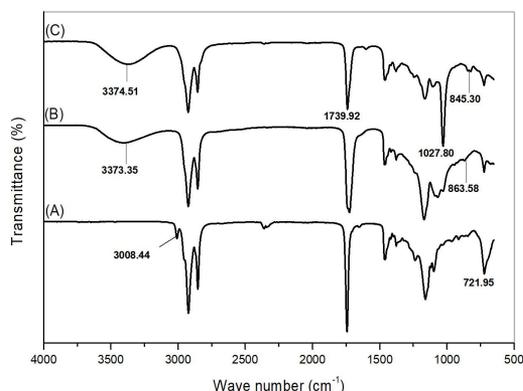
**Scheme 1.** Reaction for the synthesis of ESOME from ESO.

Schuchardt et al.<sup>[21]</sup> have reported that the overall process is a sequence of three consecutive and reversible reactions, in which di and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of ESO and 3 mol of methanol. However, an excess of alcohol is used to increase the yields of epoxidized alkyl esters and to allow its phase separation from the glycerol formed<sup>[21]</sup>.

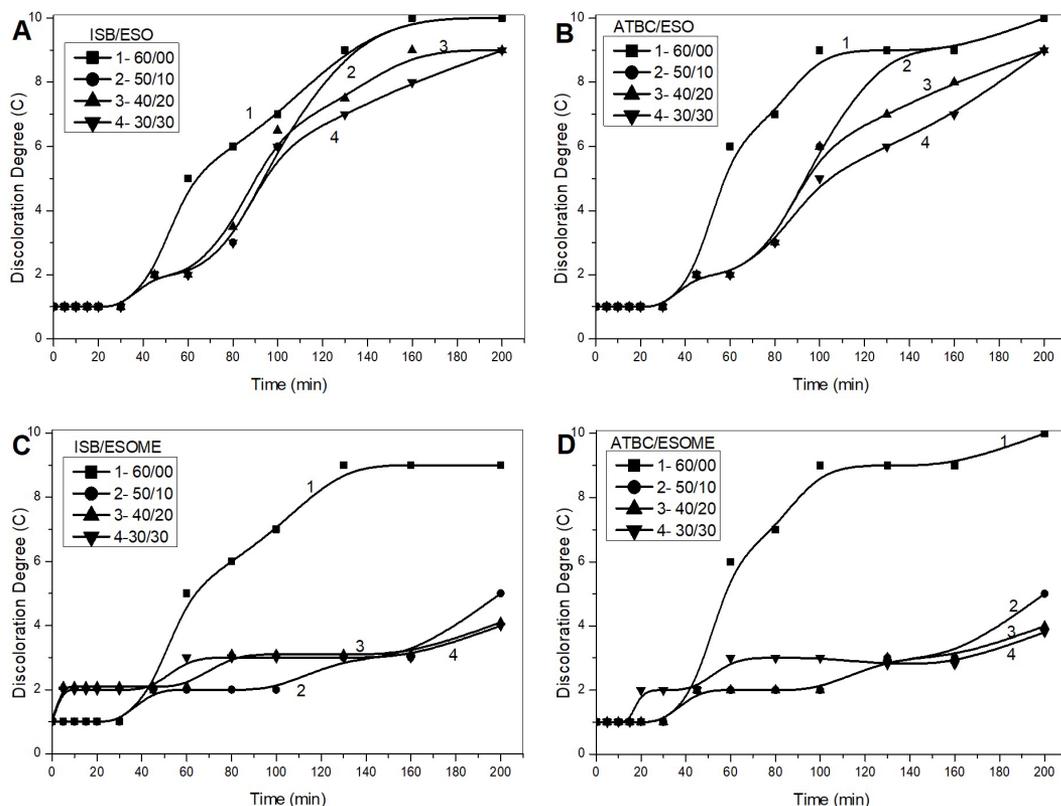
### 3.3 Fourier transform infrared spectroscopy (FTIR)

Products were characterized by FTIR (Figure 1) in order to follow the disappearance of double bonds and formation of epoxy groups. For SO, the characteristic peaks at 3008.44  $\text{cm}^{-1}$  and 721.95  $\text{cm}^{-1}$  are attributed to the stretching vibration of the double bonds  $=\text{C-H}_2$  and  $-\text{CH}=\text{CH}-$ , respectively. The FTIR spectrum displays peaks of ESO at 863.58  $\text{cm}^{-1}$  and of ESOME at 845.30  $\text{cm}^{-1}$ , characteristic of the C-O-C oxirane stretch and disappearance of the double bond at 3008.44  $\text{cm}^{-1}$ . It indicates the almost complete conversion of C=C unsaturations to epoxy groups and confirms the success of the epoxidation reaction of ESO<sup>[22,23]</sup> on fatty acid chains.

The other new peaks at 3373.35  $\text{cm}^{-1}$  for ESO and at 3374.51  $\text{cm}^{-1}$  for ESOME are attributed to the hydroxyl functional group, derived from the epoxy functional group via partial epoxy ring opening reaction. The epoxy ring opening reaction could occur either by acid catalysis in the presence of water



**Figure 1.** FTIR of (A) SO; (B) ESO and (C) ESOME.



**Figure 2.** Discoloration degree of plasticized PVC films with: (A) ISB/ESO; (B) ATBC/ESO; (C) ISB/ESOME; (D) ATBC/ESOME.

associated with aqueous solution of  $H_2O_2$  used<sup>[15]</sup>. The peak in the spectrum of ESOME at  $1739.92\text{ cm}^{-1}$  indicates the shifting of  $C=O$  absorption band and the characteristic ester band at  $1027.80\text{ cm}^{-1}$ , these results indicate that the functional group has been converted into  $-COOC-$  for the three ester functions<sup>[23,24]</sup>.

### 3.4 Discoloration sheets by static heat

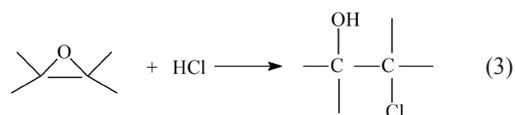
A study of coloration change is an important method for investigating the stabilizing performance of plasticizers in PVC when the variation of the PVC color from transparency towards yellow to brown then black, indicate the evolution of the degradation state of PVC sheets.

The discoloration degree of PVC samples before and after degradation was determined by using the Synmero scale. The samples are colored because of the dehydrochlorination and formation of conjugated double bonds in PVC sheets. During dehydrochlorination, HCl molecules are extracted, which initiates the formation of double bonds and polyenes in PVC chains and noticeable color change from yellow to black, when the conjugated polyene sequences contain more than four to five double bonds<sup>[25]</sup>. Figure 2 shows the discoloration degree of sheets containing different mixtures of plasticizers. All sheets turn brownish with discoloration degree ( $C \approx 5$ ) after 40 min.

The sheets containing ISB and ATBC alone were blackening after 120 minutes. But the dispersion of ESO, the degree of discoloration decreases by increasing the rate

of ESO, either mixed with ISB (Figure 2A) or with ATBC (Figure 2B) in the plasticizer system. In the case of ESOME, (Figure 2C) and (Figure 2D), the sheets have a yellow color for times in the range [0-200 minutes].

This yellowish appearance could be related to polyene formation due to dehydrochlorination of PVC with the reaction of HCl and ESOME<sup>[26]</sup>. Thus, the combination of ESO and ESOME with ISB or ATBC increases the thermal stability of formulations compared with samples containing ISB or ATBC alone. The changes in discoloration degrees for the PVC were minimal in the films plasticized in presence of ESO or ESOME. Epoxy groups of ESO and ESOME neutralize the HCl evolved by dehydrochlorination of PVC. Thus, auto acceleration of dehydrochlorination by evolved HCl is prevented because it is captured by epoxy groups, owing epoxy groups in ESO and ESOME to react with HCl, generated from PVC<sup>[27]</sup>, as shown in reaction 3.



### 3.5 Thermogravimetry analysis

Figure 3 shows the TGA and DTG curves of plasticized PVC by some plasticizer blends. The curves have similar shapes for all formulations and each one presents two distinct stages.

Table 2 summarizes the thermal performance data of plasticized PVC by the different systems in the first and second stage respectively.

The characteristic thermal parameters selected were the 1% weight loss ( $T_1$ ), which is the initial weight loss temperature, maximum degradation temperature ( $T_1$  max and  $T_2$  max), which is the highest thermal degradation rate temperature obtained from the peak of weight loss, maximum speed of degradation ( $S_1$  max and  $S_2$  max), the 5% weight loss ( $T_5$ ), the 50% weight loss ( $T_{50\%}$ )

and the residue. The elimination of a large amount of HCl happened at about 200°C. It could be attributed to the first thermal degradation stage. The second stage above 400°C is attributed to crosslinking of chains containing C=C bonds as the process of thermal degradation of polyenes involves cyclization and splitting of chains<sup>[8]</sup>. The results obtained in this range show that the PVC mixed with ATBC begins to lose weight at a lower temperature than that with ISB. However, formulations with ESO (formulation number 4, 8) or with ESOME (formulation number 11, 14) present the minimal weight loss in the first step.

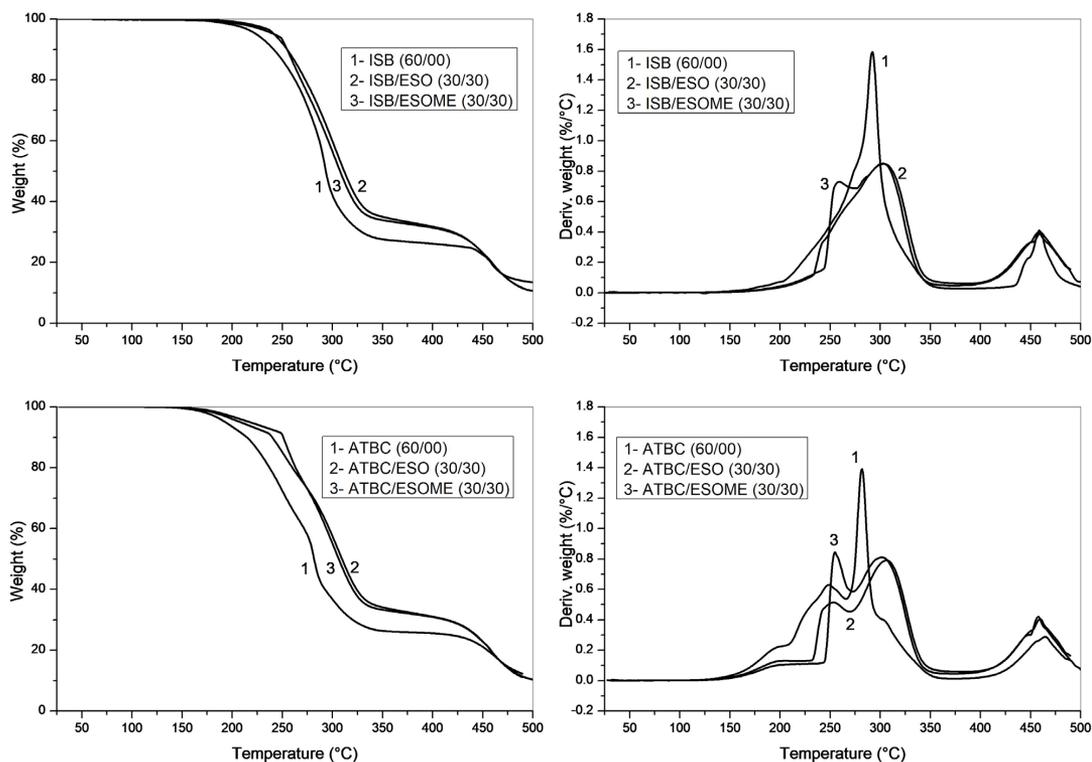


Figure 3. TGA and DTG curves for PVC plasticized with ISB, ATBC and their blends with 30 phr of ESO and ESOME.

Table 2. Thermal gravimetric analysis (TGA) results of the formulations.

Formulation number	First stage					Weight loss (%)	Second stage		Residue at 480 °C (%)
	$T_1$ (%)	$T_1$ max (°C)	$S_1$ max (%/°C)	$T_5$ (%)	$T_{50\%}$ (°C)		$T_2$ max (°C)	$S_2$ max (%/°C)	
1	184.0	292.2	1.58	224.2	293.4	73.4	458.7	0.41	13.8
2	193.1	293.4	1.12	230.7	297.5	72.1	459.3	0.35	11.0
3	196.9	297.6	0.84	235.6	304.1	69.0	459.7	0.38	11.3
4	204.0	302.8	0.85	241.9	311.6	67.0	457.3	0.39	11.6
5	160.9	281.8	1.39	193.0	281.8	74.1	465.4	0.29	12.3
6	165.4	284.7	0.87	198.8	290.5	72.2	461.1	0.34	10.9
7	165.8	303.3	0.75	201.4	303.4	69.0	460.7	0.37	11.2
8	168.9	305.7	0.79	208.0	309.4	67.2	459.2	0.40	11.1
9	196.0	292.4	1.18	231.6	296.5	72.3	459.9	0.33	10.8
10	197.8	295.5	0.95	237.0	301.8	69.5	460.1	0.37	11.1
11	198.0	302.0	0.85	242.1	307.5	67.0	460.4	0.39	11.3
12	164.3	285.4	1.00	196.8	288.5	73.0	459.8	0.35	9.9
13	167.0	252.1	0.90	203.9	300.8	69.5	461.0	0.38	11.2
14	172.3	254.4	0.84	217.2	306.1	67.7	457.5	0.42	11.2

In the first step, the presence of 30 phr ESO or ESOME with 30 phr ISB or with 30phr ATBC Instead of 60 phr ISB or 60 phr ATBC retards the temperature at 5% weight loss from respectively 224.2°C and 193.0°C to 241.9°C and 208.0°C and decreases the weight loss from 73.4% and 74.1% to 67.0% and 67.2% respectively. These results are in agreement with those of Joseph et al.<sup>[28]</sup>. From Table 2, it could be observed that the value of  $T_1$  max increases with the addition of ESO or ESOME in the plasticizer system. On the other hand,  $S_1$  max decreases.

The second stage of the degradation begins at temperatures higher than 400°C. Thermal degradation of the polyene sequences occurring during this stage yields volatile aromatic and aliphatic compounds by the intermolecular cyclization of the conjugated sequences<sup>[13]</sup>.

However, the second degradation stage occurs without any marked variation in the temperature range. Hence, ESO and ESOME improve the thermal stability of PVC blends better than ISB or ATBC.

### 3.6 Differential scanning calorimetry (DSC)

The glass transition temperature ( $T_g$ ) of all the sheets with various plasticizer combinations was determined by using differential scanning calorimetry (DSC).

This temperature is an important parameter in polymer characterization to evaluate the plasticizing effect of plasticizers mixtures added to polymer systems. DSC curves of the realized formulations are displayed in Figure 4.

The analyzed plasticized PVC sheets show  $T_g$  values ranging between 62.1°C and 65.5°C. Unplasticized PVC exhibits a glass transition temperature ( $T_g$ ) at 81.0°C. We have

observed that with incorporation of plasticizers systems,  $T_g$  values decrease steadily down to 65°C. This indicates the excellent plasticizing effect of plasticizers mixtures for 60 phr by weight<sup>[29]</sup>.

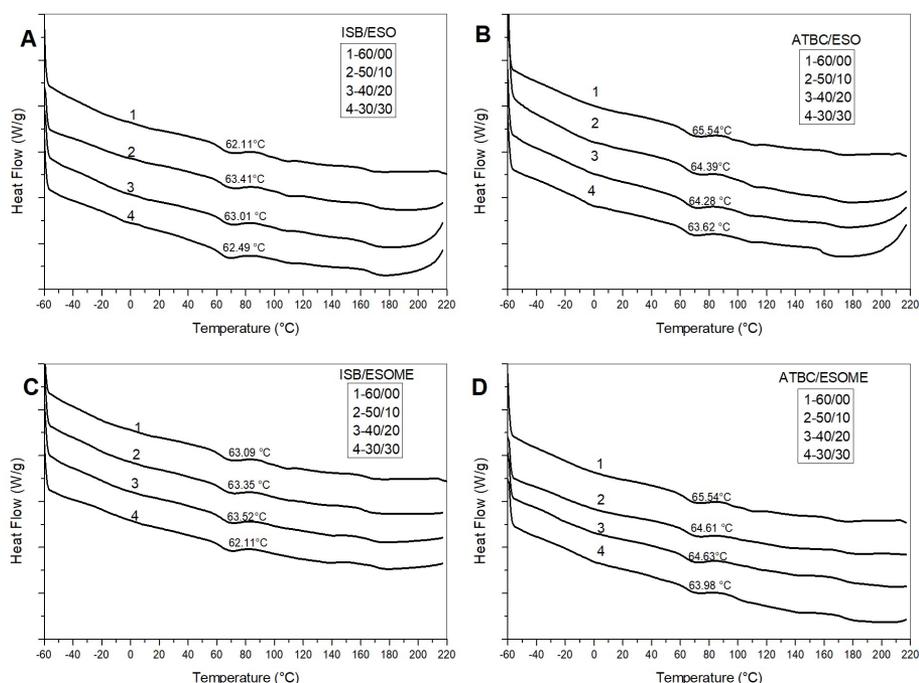
The data displayed in Figure 4 indicates that  $T_g$  values evolve slightly with ISB or ATBC and when ESO or ESOME quantity is increased from 10 to 30 phr in plasticizer system, which is agreement with a good miscibility of ISB, ATBC, ESO and ESOME with PVC.

A low value is observed for the ATBC alone (65.5°C) but it even decreases by addition of ESO or ESOME at 30 phr to 63.6°C and 64.6°C respectively. Another low value is obtained for ISB alone (62.1°C) and it increases slightly by adding ESO and ESOME from 10 phr to 20 phr. These data observations suggest that the length of the alkoxy group plays a critical role in controlling the available free volume, as it has been reported by Stuart et al.<sup>[29]</sup>.

### 3.7 Dynamic mechanical thermal analysis (DMTA)

DMTA was used to investigate the compatibility of the plasticizers with PVC. Generally, for an immiscible blend, the  $\tan \delta$  curve shows a large peak. For a highly compatible plasticizer system, the curve shows a narrow peak<sup>[14,30]</sup>.  $\tan \delta$ , loss modulus ( $E''$ ) and FWHM (full width at half maximum)<sup>[31]</sup> of realized formulations are displayed in Table 3.

The DMTA data indicate that the  $T_\alpha$  peak shifts to lower temperature when increasing concentrations of ISB or ATBC in the plasticized blends (Figure 5). Based on the data in Table 3, for example, the  $T_\alpha$  peak for the ISB/ESO system decreases from 23.0°C to 11.4°C when the ISB concentration increases from 30 to 60 phr respectively. The variation of  $T_\alpha$  is a very important factor in the evaluation of the

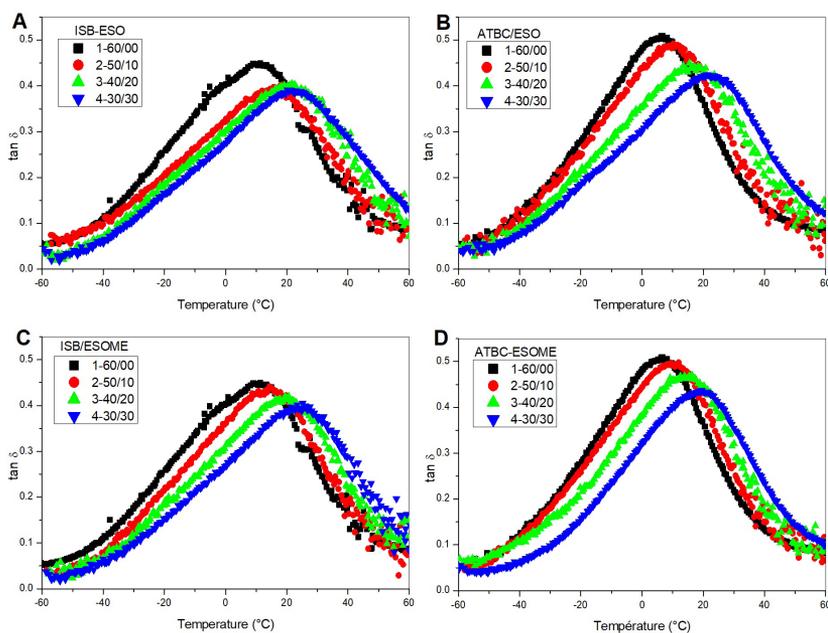


**Figure 4.** DSC curves of plasticized PVC films with: (A) ISB/ESO; (B) ATBC/ESO; (C) ISB/ESOME; (D) ATBC/ESOME.

**Table 3.** DMTA analysis of T drawn from E'' peak (°C), FWHM (°C), T $\alpha$  at different frequencies and the activation energy of PVC films with mixtures of plasticizers.

Formulation Number	T from E'' (°C)	FWHM (°C)	T $\alpha$ (°C)				Activation Energy E $\alpha$ kcal. mol <sup>-1</sup>
			1 Hz	3 Hz	5 Hz	10 Hz	
1	-30.6	51.6	11.4	15.6	18.4	19.0	45.02
2	-28.9	52.7	18.3	-	-	-	-
3	-27.1	58.5	21.7	-	-	-	-
4	-23.3	60.6	23.0	31.6	33.5	35.7	30.88
5	-33.8	45.1	6.8	12.7	13.7	15.9	39.10
6	-31.6	48.9	10.2	-	-	-	-
7	-29.7	53.0	17.2	-	-	-	-
8	-25.8	54.8	21.6	27.5	30.9	35.0	30.50
9	-27.1	52.7	14.1	-	-	-	-
10	-24.1	53.0	19.9	-	-	-	-
11	-22.0	56.8	23.4	28.7	30.3	35.3	35.70
12	-32.9	47.3	11.1	-	-	-	-
13	-30.8	47.4	15.0	-	-	-	-
14	-17.2	49.4	19.5	23.1	24.7	28.3	46.57

FWHM: Full width at half maximum.



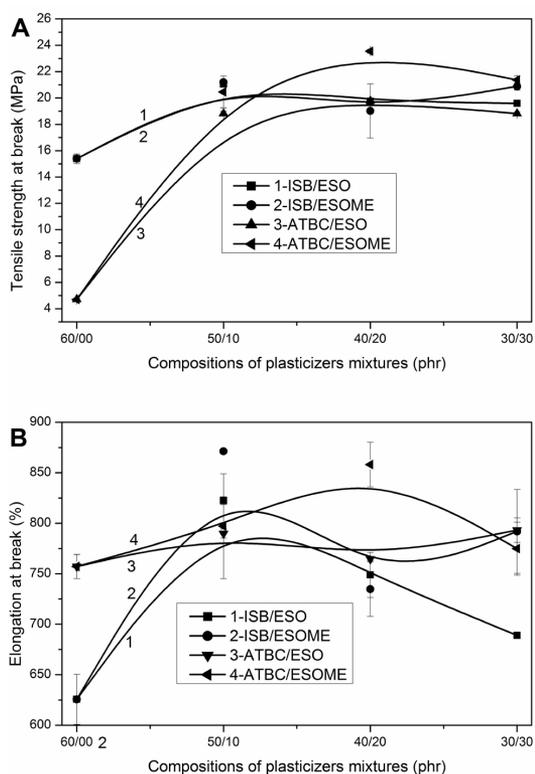
**Figure 5.** tan  $\delta$  peaks of PVC films plasticized with various plasticizers mixture (A) ISB/ESO; (B) ATBC/ESO; (C) ISB/ESOME; (D) ATBC/ESOME.

plasticizer effect and it can be seen that the T $\alpha$  values of formulations with 60 phr ISB or 60 phr ATBC are 11.4°C and 6.8°C, respectively.

This means that all the plasticizers mixtures show good plasticization of PVC. The T $\alpha$  values with 60 phr ATBC or 60 phr DOP (not shown) based formulations are very close with little difference on each other (1.8°C). However, it is known that DOP is dangerous for human health<sup>[30]</sup>, so ATBC is a potentially less toxic plasticizer for PVC based compositions. Table 3 shows that the FWHM values of PVC with ATBC and ISB alone are smaller than the FWHM values of plasticized systems with ESO and

ESOME secondary plasticizers. When ISB and ATBC content increases in plasticizer systems, the FWHM values decrease; this indicates the good compatibility of ISB and ATBC with PVC.

From the frequency dependence of the T $\alpha$ , the values of activation energy for the plasticized samples are calculated (Table 3). It appears that there is a dependence of the activation energy on the measured T $\alpha$ . It can be related to the good compatibility between PVC with ISB/ESO, ATBC/ESO and ISB/ESOME. The points corresponding to the plasticized PVC samples are shifted toward lower values of activation energy<sup>[9]</sup>.



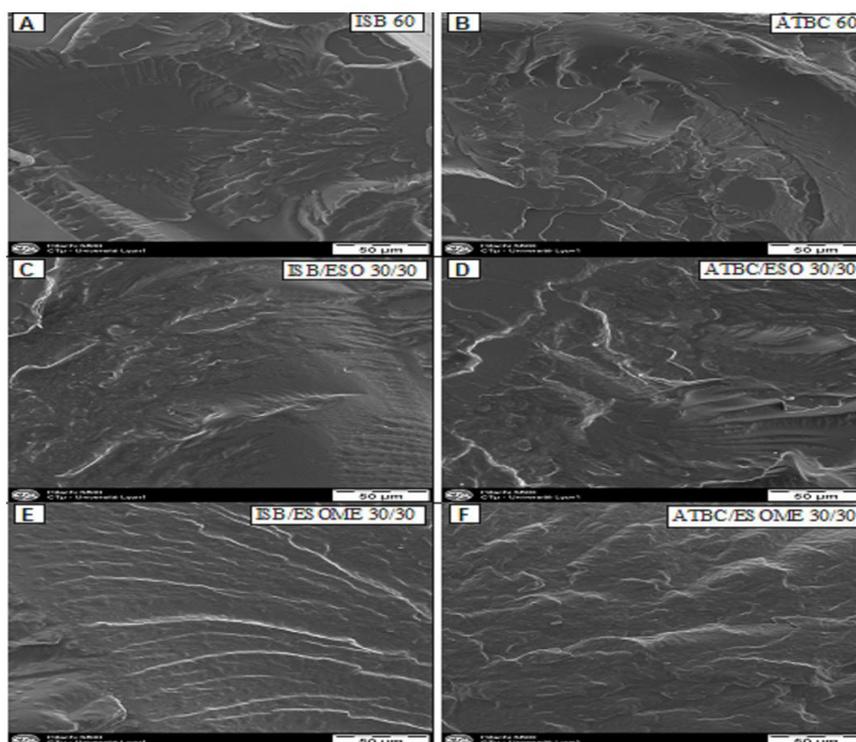
**Figure 6.** Mechanical properties of plasticized PVC films: (A) Tensile strength (Mpa); (B) Elongation at break (%).

### 3.8 Mechanical properties

Figure 6 shows the effect of the plasticizers compositions on tensile strength and elongation at break of PVC formulations. The tensile strength decreases by rising the amount of ISB or ATBC in the plasticizers systems, whereas the elongation at break increases with a rise in content of ESO and ESOME from 0 to 20 phr in plasticizer systems. The increase in tensile strength and decrease in elongation at break with 30 phr of ESO or ESOME in plasticizers systems is attributed to the increased polarity of the plasticizer, which growths the cohesive energy density (intensity of intermolecular attractions), so that with a higher polarity, materials tend to hold themselves together more tightly<sup>[32]</sup>. As a result, the chain mobility and thus the flexibility of the compounds are reduced, although the increase in tensile strength and decrease in elongation at break with ESO plasticizer may be attributed to its high viscosity. Reduction in tensile strength with an increase in ATBC or ISB content (60 phr) possibly result from a high plasticization efficiency compared to the one of other plasticizers<sup>[33]</sup>, which allows facile sliding of polymer chains past each other<sup>[32]</sup>. Hence, compounds of ATBC/ESOME (40/20) and ISB/ESOME (50/10) give the highest elongation at break 858% and 871% respectively.

### 3.9 Scanning electron microscopy (SEM)

Fractured surfaces of the selected formulations were investigated by SEM. The microscopic structures of PVC films plasticized with different plasticizers mixtures are displayed in Figure 7. A homogeneous and regular aspect



**Figure 7.** SEM micrographs of fracture surfaces of PVC films with different plasticizer compositions: (A) ISB 60 phr; (B) ATBC 60 phr; (C) ISB/ESO 30/30; (D) ATBC/ESO 30/30; (E) ISB/ESOME 30/30; (F) ATBC/ESOME 30/30.

has been obtained, without presence of PVC aggregates, when ISB or ATBC are used alone or with ESO and ESOME (30/30), which indicates a good miscibility between PVC and plasticizer systems, responsible for the higher levels of mechanical performances of films<sup>[34]</sup>. The obtained surfaces are rather homogeneous and smooth with little roughness.

This influence on the morphology of plasticized mixtures (with ISB, ATBC, ESO and ESOME) can be attributed to a decrease in the matrix viscosity and denotes a good dispersion of plasticizers in the PVC matrix<sup>[35]</sup>.

#### 4. Conclusions

Discoloration change as well as thermal degradation decreases when increasing the amount of ESO or ESOME from 10 to 30 phr in plasticized systems. The effect of the four plasticizers systems on the glass transition temperature of PVC is similar, lowering T<sub>g</sub> from 81°C for unplasticized PVC to values in the range [62°C, 65°C] for PVC specimens plasticized with different plasticizers systems. T<sub>α</sub> and FWHM decrease when increasing the amount of ISB or ATBC; which indicates they have a good compatibility with PVC. Tensile strength at break of PVC formulations with different plasticizers mixtures remains about constant by decreasing the ESO or ESOME level from 30 to 10 phr, the elongation at break is rather stable with ESO or ESOME levels from 20 to 10 phr.

The analysis of the morphology indicates that all the plasticizers have good compatibility with PVC.

ATBC or ISB with 10 to 30 phr of ESO or ESOME are good candidates to substitute phthalates such as DEHP in flexible PVC formulations.

The use of secondary biobased plasticizers, such as ESO and ESOME with other primary biobased plasticizers as ISB and ATBC is a good way for the production of flexible PVC with low health toxicity and low environmental impacts.

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