

## Thermal and Mechanical Properties of a Polyhydroxyalkanoate Plasticized with Biobased Epoxidized Broccoli Oil

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**ABSTRACT:** Broccoli oil was epoxidized through a simple process with performic acid generated *in situ* without any metal catalyst. The resulting epoxidized broccoli oil (EBO) was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, Fourier transform infrared spectroscopy, and mass spectroscopy and after a 72-h reaction, and all initial double bonds were epoxidized without further degradation of the triglyceride. EBO was used thereafter as an additive in the formulation of polyhydroxyalkanoate (PHA) films. The effects of EBO on the thermal and mechanical properties of PHA were studied with chromatography combined with thermal and mechanical analysis. From static and dynamic mechanical characterizations of PHA/EBO blends, EBO could be considered a good plasticizer for PHA. When blended with PHA, EBO caused a decrease in the elastic modulus, an increase in the elongation at break, and a decrease in the glass-transition temperature. The beneficial effect of EBO on the thermal stability of the PHA was confirmed by thermogravimetric analysis combined with size exclusion chromatography. The water vapor permeability of the PHA-containing EBO films was also controlled by the EBO content. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39983.

**KEYWORDS:** biopolymers and renewable polymers; lipids; mechanical properties; plasticizer; thermogravimetric analysis (TGA)

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### INTRODUCTION

Polyhydroxyalkanoates (PHA) are biodegradable thermoplastics obtained from fermentation processes with a wide variety of bacteria.<sup>1</sup> Because of their ecological safety, PHAs should find several applications in the manufacturing of “green” materials, both biodegradable materials and those obtained from renewable resources.<sup>2</sup> Nevertheless, compared to conventional synthetic polymers based on fossil fuels, PHAs present some major drawbacks:<sup>3,4</sup>

- They have higher costs.
- They are subject to degradation during their processing and storage.<sup>5</sup>
- They have relatively poor mechanical properties (brittleness)<sup>1,6</sup>

To increase the mechanical properties, PHAs can be blended with plasticizers. By decreasing intermolecular forces between polymer chains, the plasticizer causes increases in the flexibility, ductility, and extensibility of the final material, which can thus be processed in many different applications.

On the other hand, lubricants and stabilizers are generally used to overcome thermal and oxidative instabilities that occur mainly during transformation processes.

These concerns result in the choice of epoxidized vegetable oils (EVOs) to increase both the mechanical properties and thermal stability of PHA products. Indeed, vegetable oils are renewable raw materials that have already been used as high-temperature lubricants and also as plasticizers for conventional polymers.<sup>7</sup> Vegetable oils possess good lubricity, low volatility, a high viscosity index, and good miscibility with other fluids. To increase their thermal and oxidative properties, such vegetable oils are generally epoxidized before their use as plastic additives. EVOs are often used in the manufacturing of several kinds of plastics.<sup>8</sup> EVOs are thus described as plasticizers or coplasticizers and are used in the manufacturing of conventional petroleum-based polymers such as poly(vinyl chloride) (PVC) or, more recently, blended with biodegradable polymers such as PHAs.<sup>9,10</sup> The most well-known example is definitely epoxidized soybean oil (ESO), which has been blended with PVC for several decades<sup>11,12</sup> because of its ability to overcome brittleness through

**Table I.** Fatty Acid Composition of the BO

A <sup>a</sup> :B <sup>b</sup>	Fatty acid		Relative percentage in BO
	Name (unsaturation location)	Formula	
22:1	Erucic (13 cis <sup>c</sup> )	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>11</sub> CO <sub>2</sub> H	39.7
18:1	Oleic (9 cis <sup>c</sup> )	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	22.7
18:2	Linoleic (9 cis, 12 cis)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> CH=CH) <sub>2</sub> (CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	14.2
18:3	Gamma linolenic (9 cis, 12 cis, 15 cis)	CH <sub>3</sub> (CH <sub>2</sub> CH=CH) <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	8.1
20:1	Gadoleic (9 cis)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	7.5
16:0	Palmitic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CO <sub>2</sub> H	3.8
24:1	Nervonic (15 cis)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>13</sub> CO <sub>2</sub> H	1.0
18:0	Stearic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CO <sub>2</sub> H	0.8
20:0	Arachidic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CO <sub>2</sub> H	0.5
20:2	Eicosadienoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> (CH <sub>2</sub> CH=CH) <sub>2</sub> (CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	0.5
22:0	Behenic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>20</sub> CO <sub>2</sub> H	0.5
20:3	Eicosatrienoic (11 cis, 14 cis, 17 cis)	CH <sub>3</sub> (CH <sub>2</sub> CH=CH) <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CO <sub>2</sub> H	0.3
16:1	Palmitoleic (9 cis)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	0.2
24:0	Lignoceric	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>22</sub> CO <sub>2</sub> H	0.2
16:2	Hexadecadienoic	Undifferentiated isomers	0.1

<sup>a</sup>Number of carbon atoms.

<sup>b</sup>Number of unsaturated bonds.

<sup>c</sup>The most present.

coplasticization but also to increase the thermal stability of PVC, in particular, when used in association with metal salts or soaps.<sup>12,13</sup>

The objective of this study was to develop a new biobased plasticizer with epoxide groups obtained from broccoli oil (BO). Actually, BO is a byproduct generated during the manufacturing of a food complement extracted from the broccoli bean. This oil is disposable in great quantities with a relatively low initial cost. At the same time, PHAs are biobased and biodegradable polymers obtained by fermentation from renewable resources. Thus, this would be the first effort to develop a new kind of plastic additive that would also be biobased and noncotoxic to produce a fully green material.

Compared to oils conventionally used in material processing,<sup>9,14,15</sup> BO is rich in long-chain fatty acids (Table I) and especially erucic acid; this can afford plasticizers with interesting new properties, such as a better ability to increase free volume in materials through higher steric hindrance. Furthermore, BO contains an average of four unsaturations, whereas conventional oils, such as palm or olive oils,<sup>15</sup> only contain two or three, which afford more sites for epoxidation.

In this study, the epoxidation process of BO was first described, and the efficiency of the reaction was determined through <sup>1</sup>H-NMR, Fourier transform infrared (FTIR) spectroscopy, and mass spectroscopy (MS) techniques. Afterward, we focused on the efficiency of the modified BO in the improvement of the thermal stability and mechanical properties of PHA blends. Water vapor permeability (WVP) was also recorded as a function of the epoxidized broccoli oil (EBO) content in the PHA films.

## EXPERIMENTAL

### Materials

The PHA, a poly(3-hydroxybutyrate-co-3-hydroxyvalerate), containing 8% mol of hydroxyvalerate, was purchased from Tianan Biologic (China) under the trade name of Enmat Y1000P (weight-average molecular weight = 340,000, polydispersity index (PI) = 2.53). BO was kindly supplied by Sojasun Technologies. Its composition in fatty acids is given in Table I. NMR spectra were recorded at 400 MHz (<sup>1</sup>H-NMR) and 100 MHz (<sup>13</sup>C-NMR). The chemical shifts ( $\delta$ ) are reported as parts per million referenced to the appropriate residual solvent peak. The coupling constants are reported in hertz. The data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens, attribution). The abbreviations used are as follows: dd (doublet of doublet) and m (multiplet). The mass spectra were recorded on a Shimadzu LCMS 2020 spectrometer. Methanol was used as eluant, and ESI (electrospray) mode was used for ionization. Ions were detected as [M + Na]<sup>+</sup> where M represent the molecular mass of the molecule.

### Preparation of the EBO

The BO was epoxidized at 40°C with performic acid generated *in situ* in a biphasic medium (toluene/water). The molar ratio of hydrogen peroxide/formic acid/BO unsaturations was 20/2/1. All of the reagents were analytical grade and were used as received from the supplier (Acros). BO, toluene, and formic acid were mixed into a reactor with sufficient stirring. Hydrogen peroxide (30 wt % in water) was added dropwise to the reaction mixture at 20°C, and the temperature was raised to 40°C. The reaction was monitored by MS, and after 72 h at the

same temperature, the aqueous phase was extracted twice with toluene, and the combined organic phases were dried ( $\text{MgSO}_4$ ). The solvent was then evaporated under reduced pressure. The EBO was characterized by NMR (J for coupling constant), MS ESI (electrospray), and FTIR spectroscopy (see the Results and Discussion section for details).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz,  $\delta$ , ppm): 0.79–1.01 (m, 9H,  $\text{CH}_3$ ), 1.18–1.77 (m, 86H,  $\text{CH}_2$ ), 2.22–2.27 (m, 6H,  $\text{CH}_2\text{-C=O}$ ), 2.82–3.15 [m, 7.8H (3.9 epoxides per molecule), epoxides], 4.07 (dd,  $J$  (J for coupling constant) = 5.9, 11.9 Hz, 2H,  $\text{CH}_2\text{-O}$ ), 4.22 (dd,  $J$  = 4.4, 11.9 Hz,  $\text{CH}_2\text{-O}$ ), 5.17–5.22 (m, 1H,  $\text{CH-O}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz,  $\delta$ , ppm): 14.0 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 24.8 ( $\text{CH}_2$ ), 26.6 ( $\text{CH}_2$ ), 27.9 ( $\text{CH}_2$ ), 28.9–29.7 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 34.0 ( $\text{CH}_2\text{-C=O}$ ), 54.1 (epoxides), 56.7–57.2 (epoxides), 62.1 ( $\text{CH}_2\text{-O}$ ), 68.9 ( $\text{CH-O}$ ), 172.8–173.3 ( $\text{C=O}$ ).

### Preparation of the PHA/EBO Blends

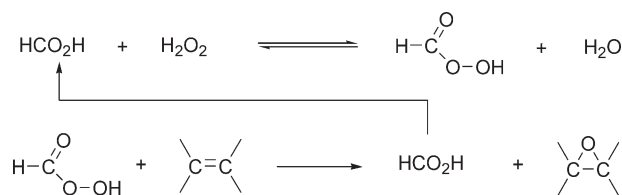
PHA-based polymers films with different EBO contents were prepared by extrusion (Brabender plasticorder, single screw 19:25 D (D is for diameter and corresponds to the length/diameter ratio)) through a flat die [Length ( $L$ ) = 150 mm, film thickness ( $e$ ) = 200  $\mu\text{m}$ ] before being conformed and wound with a thermoregulated calendar (calendar temperature = 45°C, Brabender Univex), which was used to take off, cool, and wind up the film to a thickness of 200  $\mu\text{m}$ . All of the processed samples were then stored at 23°C under 50% relative humidity (RH) for at least 4 days before further characterization.

### Characterization

**Molar Mass Distribution Analysis.** The PHAs were analyzed by size exclusion chromatography (SEC) to determine their molar mass distributions. This characterization was performed with a set of three columns: 2 ResiPore and 1 PL gel Mixed C (Polymer Labs.). The detection system was composed of a refractometer and a UV detector. Chloroform was used as eluant with a flow rate of 0.8 mL/min. The elution profiles were analyzed by Empower gel permeation chromatography module software (Waters). Calculations were based on calibration curves obtained from polystyrene standards ranging from 200 to  $6 \times 10^6$  g/mol. For the analysis, samples were prepared from PHA-based films obtained by the extrusion process detailed previously. Each film was dissolved in hot chloroform, and the solution was injected after filtration.

**Stress–Strain Testing.** Tensile tests were carried out in a controlled atmosphere at 23°C with an RH of 48% according to ISO 527 with an Instron 5566A apparatus. The loading speed was 5 mm/min. An Instron extensometer was used with a nominal gauge length of 25 mm. The tests were carried out at least five times for each material, and the results were averaged arithmetically.

**FTIR Spectroscopy.** For IR spectroscopy, a PerkinElmer Spectrum 100 system IR spectrometer was used in attenuated total reflectance mode with a DTGS (deuterated triglycine sulfate) detector (4- $\text{cm}^{-1}$  resolution) with the spectral range 650–4000  $\text{cm}^{-1}$ . In these measurements, 15 scans were applied, and the data were collected and analyzed with Spectrum ES 5.0 software. The sample was placed onto the surface of a diamond prism,



**Figure 1.** Epoxidation of BO with the *in situ* generated performic acid.

and the IR radiation was collected after total reflection from the diamond–sample interface.

**WVP.** WVP of the film was studied with the Cups methods (ISO 7783). The experimental setting consisted of a cylindrical vessel filled with a desiccant powder and sealed with the investigated film. For our test, 10 g of  $\text{CaCl}_2$  was used as the desiccant powder, and the temperature was set to 23°C with an RH of 50%. This method consisted of monitoring the water mass uptake of the desiccant powder with time. The water vapor transmission rate (WVTR;  $\text{g m}^{-2} \text{s}^{-1}$ ) was then calculated from the slope of the mass uptake profile versus the time as soon as the steady state was reached. We used the following equation:

$$\text{WVP} = \frac{\text{WVTR} \times e}{\Delta p} \quad (1)$$

where WVP is the water vapor permeability coefficient ( $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ ) and  $\Delta p$  is the water vapor partial pressure difference (Pa). From the experimental conditions,  $\Delta p$  was  $1.4 \times 10^3$  Pa, as calculated for a temperature of 23°C and an RH of 50%. Four films of each polymer were tested, and the results were arithmetically averaged.

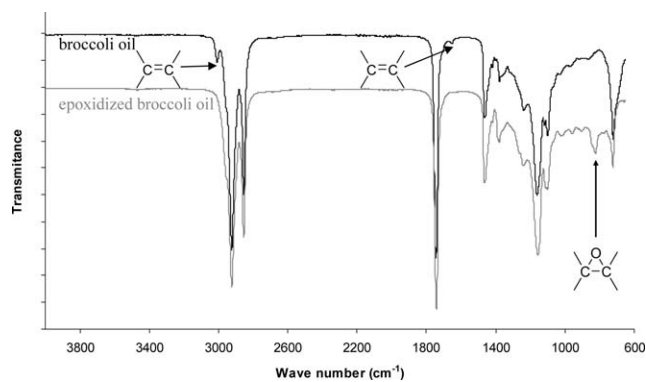
**Dynamic Mechanical Analysis (DMA).** The viscoelastic properties of the cured films were measured with a DMA instrument (Q800, TA Instruments). Rectangular specimens, 14 mm in length, 7 mm in width, and 0.20 mm in thickness, were prepared. The measurements were taken in tension mode at a frequency of 1 Hz and a strain of 0.1%. The temperature ranged from –100 to 150°C at scanning rate of 3°C/min. The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss factor ( $\tan \delta$ ) of the cured films were measured as a function of the temperature.

**Thermogravimetric Analysis (TGA).** The thermogravimetric experiments were carried out on raw pellets with a Mettler Toledo TGA/DSC 1 thermal analyzer at a scanning rate of 10°C/min under air with the temperature increasing from 20 to 700°C.

## RESULTS AND DISCUSSION

### EBO: Synthesis and Characterization

**Synthesis.** The epoxidation reaction was carried out, without any metal catalyst, with *in situ* generated performic acid with hydrogen peroxide.<sup>16,17</sup> Indeed, two reactions proceeded simultaneously (Figure 1): a reversible one, corresponding to the formation of the peracid from hydrogen peroxide and formic acid, and an irreversible one, corresponding to the epoxidation of the oil unsaturations. The recycling of formic acid permitted us to use it in a catalytic amount. This epoxidation process based on an *in situ* generated peracetic acid is the cheapest method to use at the industrial scale, and it is actually the major route of preparation of ESOs.



**Figure 2.** FTIR spectra of BO (black line) and EBO (gray line).

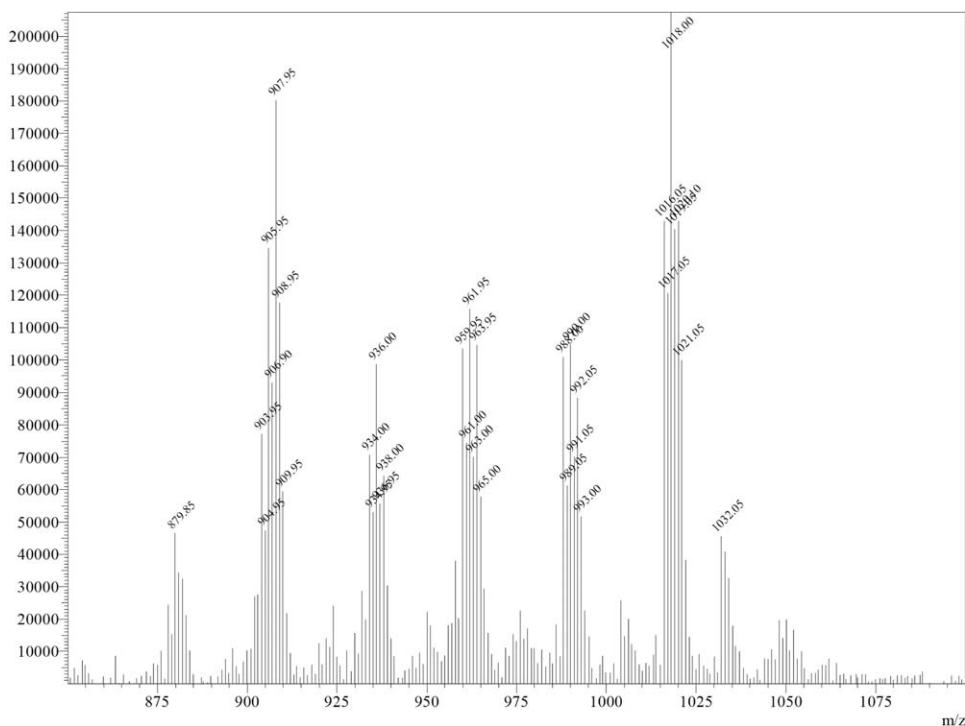
**FTIR Spectroscopy.** EBO was characterized by FTIR spectroscopy and compared to BO. EBO presented a characteristic peak at  $824\text{ cm}^{-1}$  from the epoxy group (Figure 2), which did not exist in the BO spectra. Conversely, peaks at  $1639\text{ cm}^{-1}$  ( $\nu_{\text{C}_{\text{sp}^2}\text{—H}}$ ) and  $3003\text{ cm}^{-1}$  ( $\nu_{\text{C}_{\text{sp}^2}\text{—C}_{\text{sp}^2}}$ ), attributed to the alkene, were only present in the BO spectra. All other peaks, at  $721\text{--}722\text{ cm}^{-1}$  (methylene in-phase rocking);  $950$ ,  $1020$ , and  $1098\text{ cm}^{-1}$  (ether, antisymmetric stretching);  $1156$  and  $1230\text{ cm}^{-1}$  (ester, antisymmetric stretching);  $1379\text{ cm}^{-1}$  (methyl symmetric deformation);  $1464\text{ cm}^{-1}$  (methyl antisymmetric deformation); and  $1742\text{ cm}^{-1}$  (esters aliphatic  $\text{C}=\text{O}$  stretching), were observed for both BO and EBO, and similar FTIR spectra were obtained from other vegetable oils, epoxidized or not.<sup>18</sup>

**MS/NMR.** MS (ESI) gave us access to the distribution of the chain length and to the number of epoxide functions per triglyceride. The comparative MS spectra of BO and EBO are shown on Figures 3 and 4, respectively. These clearly demonstrate that

all of the double bonds of the original oil were epoxidized without any change in the other part of the triglyceride. The different mass-to-charge ratio ( $m/z$ ) signals were assigned according to the global chain lengths and the number of unsaturations (Table II). All of the corresponding fully epoxidized triglycerides were detected on the mass spectra of EBO. According to the starting BO, the EBO triglycerides bore two to five epoxides per molecule. It was noteworthy that the oxidation of different triglycerides led to EBO triglycerides with very close  $m/z$  values. For example, the triglycerides at  $m/z = 905.8$  ( $[\text{M} + \text{Na}]^+$ ) with four double bonds and at  $m/z = 937.8$  ( $[\text{M} + \text{Na}]^+$ ) with two double bonds led to epoxidized compounds at  $969.7$  ( $[\text{M} + \text{Na}]^+$ ) and  $969.8$  ( $[\text{M} + \text{Na}]^+$ ), respectively, that were not distinguishable with a low-resolution analyzer. Additionally, the NMR analysis confirmed the absence of residual unsaturation and showed an average of 3.9 epoxides per molecules. This number of epoxide groups per molecule was rather important compared to other epoxidized oils, such as ESO, whose number of epoxide groups varied between 2.5 and 4.6 with regard to the epoxidation process.<sup>19</sup>

### Characterization of the EBO–PHA Blends

**Plasticization: Static and DMA.** To confirm that the flexibility of the PHAs could be improved by blending with EBO, the tensile properties of the PHA/EBO blends were compared with those of pure PHA. The blends of PHA with different proportions of EBO were used to prepare  $200\text{ }\mu\text{m}$  thick films, as detailed in the Experimental section. Stress–strain tests were performed on EBO-plasticized PHA films, and for each sample, the elongation at break and the elastic modulus were recorded. Figure 5 represents the evolution of the elastic modulus and the elongation at break as a function of the EBO content for each PHA film, which ranged from 0 to 15% w/w.



**Figure 3.** MS analysis of BO ( $[\text{M} + \text{Na}]^+$ ).

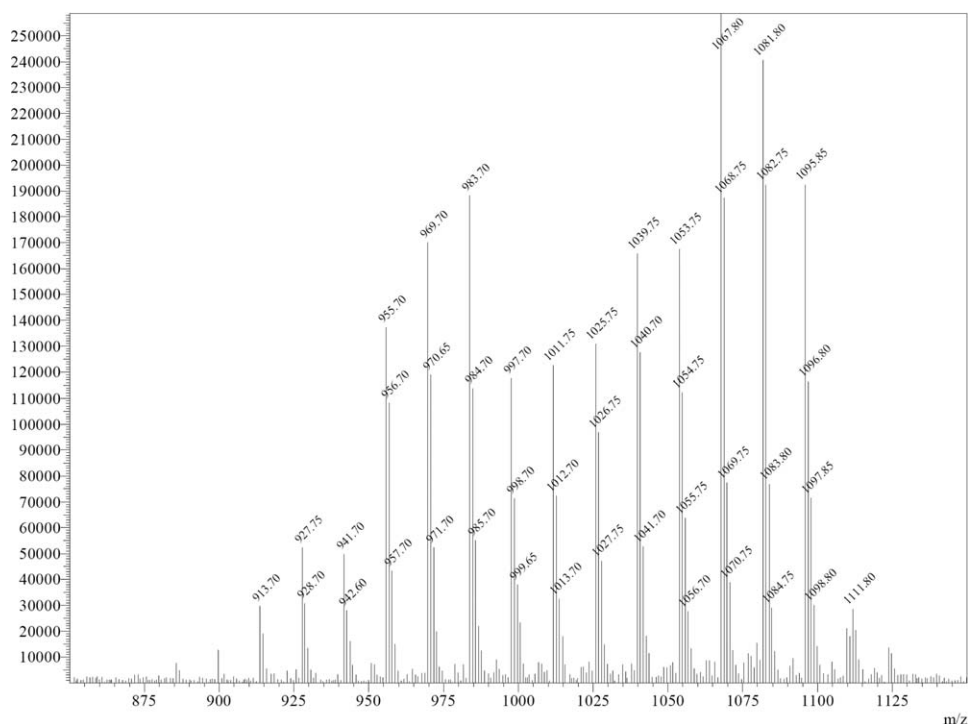


Figure 4. MS analysis of EBO ( $[M + Na]^+$ ).

Most commercial PHAs are known to be initially rather hard and brittle, as mentioned in a previous article.<sup>20</sup> This was confirmed here by the mechanical properties recorded for the unplasticized sample, which exhibited an important elastic

Table II. Starting BO Triglycerides and Corresponding Epoxidized Molecules

BO		EBO	
$m/z$ $[M + Na]^+$	N of C=C	$m/z$ $[M + Na]^+$	Nb of epoxide
877.7	4	941.7	4
879.7	3	927.7	3
881.8	2	913.7	2
903.7	5	983.7	5
905.8	4	969.7	4
907.8	3	955.8	3
909.8	2	941.8	2
933.8	4	997.8	4
935.8	3	983.8	3
937.8	2	969.8	2
959.8	5	1039.8	5
961.8	4	1025.8	4
963.8	3	1011.8	3
987.8	5	1067.8	5
989.8	4	1053.8	4
991.9	3	1039.9	3
1015.9	5	1095.8	5
1017.9	4	1081.9	4
1019.9	3	1067.9	3

modulus of 2800 MPa for an elongation at break of only 1.38%. When EBO was added to the blend, the elastic modulus was drastically reduced to about 2200 MPa for an EBO content of only 5% w/w. A further increase in the EBO content still caused a decrease in the elastic modulus to values lower than 1900 MPa for samples containing 15% w/w epoxidized oil. With regard to ultimate deformation, the increase in the EBO content in the PHA films caused an increase in the maximum elongation compared to the 1.38% maximum elongation of the unplasticized samples; this value increased regularly with ESO content to around 1.80% for the 15% w/w ESO containing films.

The decrease in the elastic modulus concomitant to an increase in the maximum elongation with the content of ESO confirmed that EBO could be a possible plasticizer for polyhydroxyalcanoates. With regard to a few other studies dealing with PHA

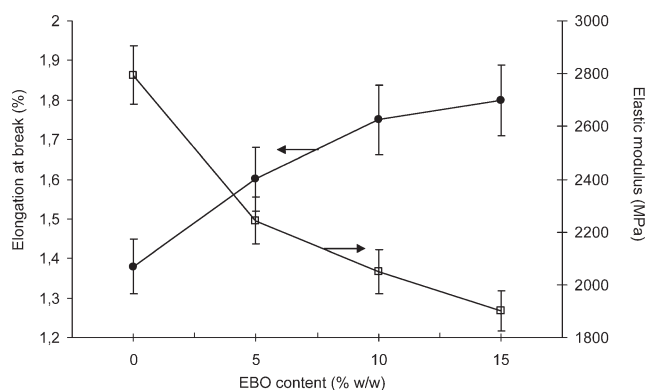
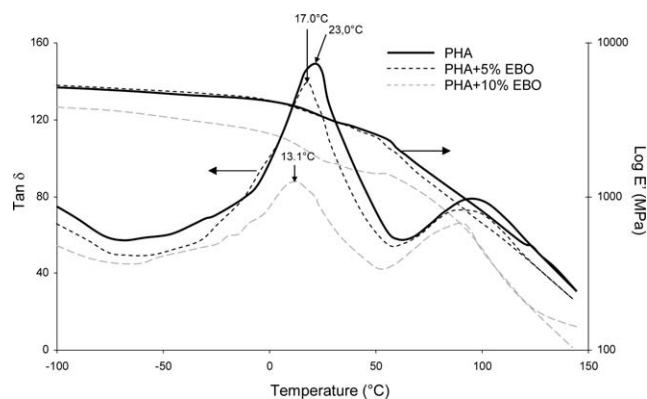


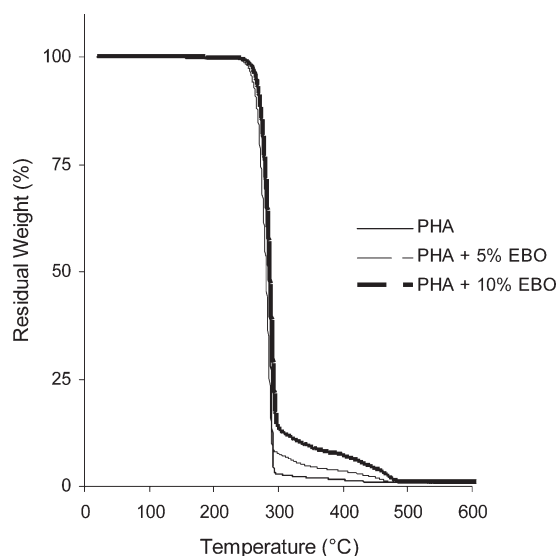
Figure 5. (□) Elastic modulus and (\*) elongation at break as a function of the EBO content in the PHA films.



**Figure 6.**  $\tan \delta$  and  $E'$  values obtained from DMA analysis at a frequency of 1 Hz and a heating rate of  $3^\circ\text{C}/\text{min}$  for the EBO-plasticized PHA films.

plasticization with epoxidized oils,<sup>9,10</sup> the plasticizing efficiency of EBO was comparable to that of ESO and showed that the initial properties of the PHAs also depended on their composition, which varied from one study to another.

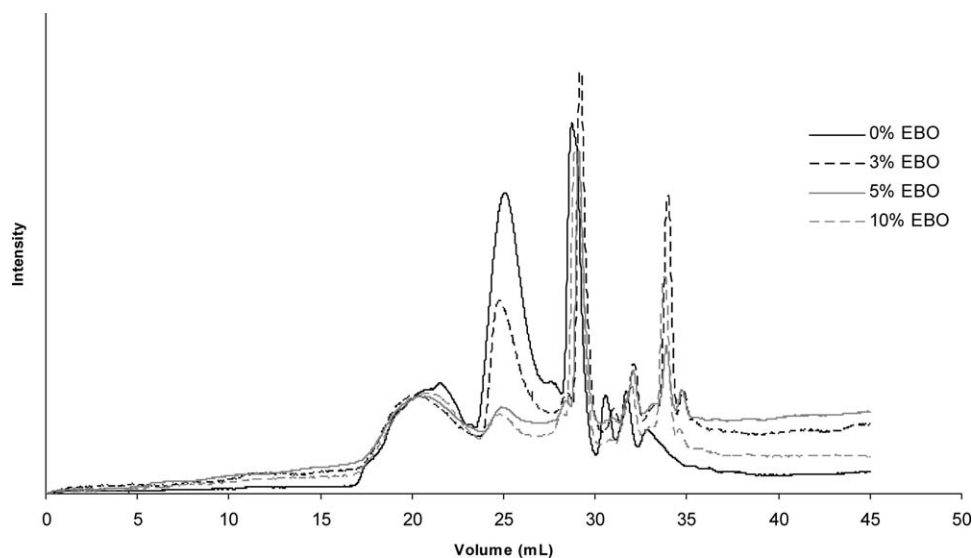
The viscoelastic transitions from brittle to rubbery state were also determined by DMA through  $E'$  and  $\tan \delta$  determination. The results are plotted in Figure 6.  $\tan \delta$  corresponded to the ratio of  $E''$  (not plotted here) to  $E'$  and is usually used to determine the energy dissipated during heating. The temperature corresponding to the  $\tan \delta$  peak was directly correlated to the glass-transition temperature ( $T_g$ ) of the material. As shown in Figure 6,  $E'$ , which measures the stored energy and represents the elastic portion, of the PHA samples decreased with EBO content, and this was noticeably visible for PHA films containing 10% w/w EBO. The increase in the EBO content caused a better mobility of the polymer chains. This led to an increase in the damping capacity of the polymer and led to a decrease in  $T_g$ . An increase in the EBO content in the PHA films caused a decrease in  $T_g$  associated with the  $\tan \delta$  peak temperature. The initial  $T_g$  of PHA without EBO, observed at about  $23.0^\circ\text{C}$ , was lowered to  $17.0^\circ\text{C}$  for films containing 5% w/w EBO and



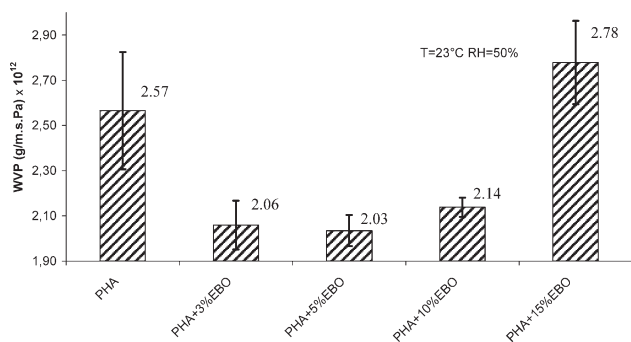
**Figure 7.** TGA thermograms of the PHA–EBO blends.

decreased further to  $13.1^\circ\text{C}$  for the sample containing 10% w/w EBO. This noticeable shift in the  $\tan \delta$  peak to lower temperatures, which indicated a decrease in  $T_g$  with EBO content, was also a proof of the plasticizing ability of the EBO toward PHA. As a comparison, Choi and Park<sup>10</sup> obtained a  $12^\circ\text{C}$  decrease in  $T_g$  for a poly(hydroxybutyrate-*co*-hydroxyvalerate) plasticized with 20% w/w ESO.

**Thermal Properties of the PHA–EBO Blends.** The thermal degradation behavior of the PHA–EBO blends was investigated with dynamic TGA. The obtained thermograms are plotted in Figure 7. The thermal degradation of pure PHA occurred through one step with an onset temperature of  $285^\circ\text{C}$ . The shapes of the curves obtained for the PHA–EBO blends featured two separate degradation steps. The first one was assigned to the PHA matrix, whereas the second one corresponded to EBO. No significant decay was observed in terms of the degradation



**Figure 8.** SEC of the PHA and PHA–EBO blends prepared by extrusion in the Brabender plasticorder.



**Figure 9.** WVP of the PHA–EBO blends (temperature  $T = 23^{\circ}\text{C}$ , relative humidity  $\text{RH} = 50\%$ ).

temperature between the pure and EBO-plasticized PHA. Thus, EBO did not act as a prodegradant additive for PHA.

Chromatograms obtained from the SEC of the PHA and PHA–EBO blends after extrusion are represented in Figure 8. With regard to the PHA chromatogram, the peak around 20 mL corresponded to the main population of polymer chains (number-average molecular weight = 190,000 g/mol, polydispersity index (PI) = 1.66), and the second peak around 25 mL can be attributed to shorter polymer chains resulting from PHA degradation (number-average molecular weight = 10,200 g/mol, PI = 1.2). From the relative observation of the two main peaks, we noticed that the intensity of the second peak clearly decreased compared to the first one as the EBO content in the film increased. This suggested that the EBO presented positive effects on the PHA thermal stability.

**WVP.** Figure 9 represents the evolution of WVP of the EBO-plasticized PHAs as a function of the EBO content. Compared to the unplasticized PHA reference sample, the EBO-containing films presented significantly different WVP values. First, for low EBO contents in the PHA films, inferior to 5 w/w %, the WVP decreased with the EBO content to reach a lower value of  $2.03 \times 10^{-12} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  (cf.  $2.57 \times 10^{-12} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for the PHA reference sample). With further increases in the EBO content in the PHA films (up to 5% w/w), the WVP increased again to reach  $2.78 \times 10^{-12} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for samples containing 15% w/w EBO.

The first WVP decrease for PHA films containing less than 5% w/w was correlated with the increase in the global hydrophobicity of the film and was related to the incorporation of the BO. Thereafter, further increases in the WVP for PHA films containing more than 5% w/w EBO were correlated to the simultaneous increases in the free volume in the material in close relation to the plasticizing phenomenon and the relative steric hindrance of the epoxidized oil. From the differential scanning calorimetry measurements, which are not presented here, no significant change in the PHA crystallinity was observed with the EBO content.

## CONCLUSIONS

The aim of this study was first to synthesize EBO and second to evaluate its plasticizing and thermal stabilizing abilities for improving the mechanical and thermal properties of PHAs.

The decrease in the elastic modulus combined with the increase in the elongation at break observed by stress–strain testing on

the PHA–EBO blends with increasing EBO content confirmed the plasticizing ability of the epoxidized oil. This was confirmed by the decreases in  $E'$  and  $T_g$  determined by DMA as the EBO content increased in the PHA/EBO blends.

The thermal stabilizing effect of EBO on PHA was confirmed by SEC and showed that ESO prevented the appearance of low-molecular-weight fragments of PHA during processing.

Finally, EBO showed its ability to control WVP of PHA; this led us to the overall conclusion that EBO would be an interesting biobased plasticizer and thermal stabilizer for PHAs (and eventually other polymers) in the manufacturing of packaging films for example.

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