

Researching of the external plasticizing and extrusion of natural fermented Polyhydroxybutyrate, and the effect of the biodegradable plasticizers in the mechanical, physical and thermal properties

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Abstract

The use of environmental biodegradable polymers is an alternative that is growing year by year, basically because in that way it is possible to reduce the great amount of plastic waste and pollution generated by the most commonly used plastics. The plasticization of the environmentally friendly poly(3-hydroxybutyrate), PHB, with five classes of biodegradable plasticizers has been studied. So far, many blends containing PHB have been studied, but only a few are totally biodegradable. Plasticizers have been recently related to environmental and health problems; for that reason it is important to investigate in the expansion of plasticizing compounds to meet new material challenges involving efficiency and economy. It is well known that the main disadvantages of the PHB are its brittleness due to the small values of breaking elongation, and its high production cost which end up in a higher cost than commercial polymers making difficult the commercial production of this material. In this report it is intended to analyze the behavior of PHB when it is plasticized with natural and biodegradable oils. From here, a reduction –mainly in the glass transition temperature, elasticity modulus and yield and tensile strengths– is expected, which would

decrease the brittleness of the material. The natural oils used in the experiments are obtained from plants and consequently the costs associated to production are cheaper if compared with biodegradable plasticizers already produced industrially. Experimental information in literature about these oils used as plasticizers is not found; therefore one of the main targets of this report is to construct a foundation of what could be the future of plasticizers and 100% biodegradable end-user materials.

Keywords: PHB, biodegradability, plasticizers, biodegradable plasticizers.

INTRODUCTION

Poly-(R)-3-hydroxybutyrate (R-PHB) is an environmental friendly bacterial polyester (1). It is part of the family of the poly(hydroxyalkanoates), PHA. The chemical structure of the PHV family can be summarized in the following structure:

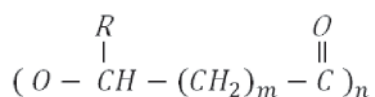
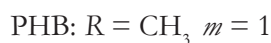


Figure 1. PHA's general structure (1).

Where R is an alkyl group of different length, n and m are integer numbers representing the following molecules for PHB (1).



i-PHB is a semicrystalline and high molecular weight biodegradable thermoplastic (2). PHB is a thermoplastic material based on naturally occurring and cheap raw materials. This specific characteristic brings to it some advantages and disadvantages when compared with other oil-derivates-thermoplastics (4). The most advantageous characteristic of this material is its biocompatibility and biodegradability, presenting microbial degradation in climatic/landscapes environmental. PHB tends to be more brittle than conventional thermoplastics, limiting its fields of application, even though mechanical properties of this biodegradable material can be compared with those of the commercially used thermoplastic isopolypropylene (i-PP) (5), (6). Other drawbacks of PHB, besides fragility, are thermal degradability at temperatures near to the range of the melting point and its high price (3) (7) (8). PHB homopolymer also crystallizes slowly when is cooled down from the melting temperature and consequentially it suffers from an increase of the embrittlement when is subjected to an aging process (9). The storage at or above room temperature induces in the polymer a logarithmic increase in crystallinity with time.

PHB is a material in which the range of commercial applications is limited, firstly, because of its thermal instability and brittleness (12) and high cost, besides

that the molecular weight of PHB decreases dramatically when the temperature is very close to its melting point. These disadvantageous properties limit widely the application of this biodegradable polymer specially in the film industry where biodegradation is preferred (5).

PLASTICIZERS

A plasticizer is a substance which is added to a polymer in order to modify the physical properties (melt viscosity, the glass transition temperature, the modulus of elasticity, its flexibility and stretchability) and improve the processability of the material when requires without altering the main chemical structure of the initial material (13). Plasticizers can be mainly classified as external and internal ones, being the external plasticizers the most commonly used. External plasticizers are low molecular weight or oligomeric molecules which are not attached to the main bond. They form secondary bonds to polymer chains and spread them apart, reducing polymer-polymer chain secondary bonding, providing more mobility for the macromolecules; thus changes in elastic properties of PHB/low molecular weight plasticizer are due to the efficient weakening of intermolecular interactions in the amorphous regions of the polymer

The right use and effectiveness of a plasticizer depends basically on the next parameters (15):

Compatibility: Indicates the mutual solubility of polymer/plasticizer system.

Permanence: Polymer must retain the plasticizer under different environmental conditions.

Efficiency: This term refers to the amount or concentration of plasticizer to give a certain degree of flexibility.

Plasticizers should have common features in the chemistry: the functionality which is slightly to strongly polar for compatibility with the polar polymer (aromatic, ester groups) and a non polar functionality for internal lubrication (hydrocarbons). The polar portion of the plasticizer provides the attractive force necessary to attach to the polymer chain, so in that way the plasticizer is attached to the polymer in the points of polar attraction, whereas the non polar or hydrocarbon region which is not attractive act as a lubricant between polymer chains (16).

Plasticizers for biodegradable polymers are to be preferred also biodegradable. When disposed in biologically active environments, biodegradable polymers are completely converted to biological products (biogas, humid matter, biomass, etc.) within a certain period. These polymers, as well as their degradation products, must cause no important effects on the environment. In this point most of the plasticizers used in synthetic polymers are not suitable for PHB. In this field health and safety issues dominate the researching where are more demanding requirements though, since by definition they will be released to the environment during normal product use.

For the reasons stated above and with the idea of generate a general screening of the physical and mechanical properties of new natural and biodegradable plasticizers in PHB it was decided to use a biodegradable plasticizer like citric acid ester as a main reference due to its demonstrated efficiency in thermoplastics (13) (16) and four types of plant oils such as soybean, olive, safflower and rapeseed oils, as main plasticizers. These refer to fatty acid esters as plasticizers. Researching on a plasticization of the latter materials is scarce on literature and only experiments with soybean oil as plasticizer were found (19), (1).

MATERIALS

Plasticizers

Citric acid esters (as control)

Citric Acid (2-Hydroxy-1,2,3-propanetricarboxylic acid, in IUPAC naming) is a colorless crystalline organic compound belonging to carboxylic acid family. It exists in all plants (especially in lemons and limes) and in many animal tissues and fluids. Triethyl Citrate is used as a high boiling solvent and plasticizer for vinyl resins, cellulose acetates. It is a plasticizer allowed in the field of food additive, food contact material, and medical and pharmaceutical products.

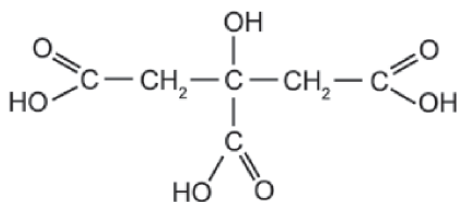


Figure 2. Citric acid molecule (21).

Natural oils

The general chemical structure of natural oils is obtained from one molecule of glycerol (Figure 3) and three fatty acids (Figure 4). An example of this can be seen in Figure 5 where the structure of olive oil is presented. Olive oil consists of two radicals of oleic acid and one of palmitic acid attached to glycerol. For this report 4 types of natural oils were tested as natural plasticizers: rapeseed oil, olive oil, safflower oil and olive oil.

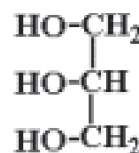


Figure 3. Glycerin structure (24).

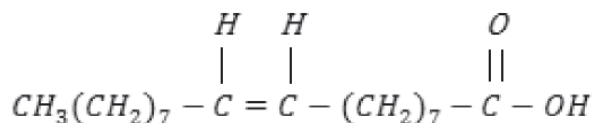


Figure 4. Oleic acid structure (24).

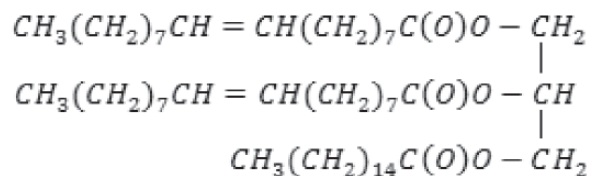


Figure 5. Olive oil structure (24).

EXPERIMENTAL METHODS AND DISCUSSION

Determination of miscibility and compatibility between a plasticizer and a polymer resin can be realized in several ways: From the analysis of the glass transition temperature in the blended system, from density measurements, from infrared spectroscopy, from morphology, from wide and small angle X-ray scattering, and others (3). In this report four main experimental methods were developed:

- Kneading or internal mixing of PHB/plasticizers, where the analysis of the relationship time/torque determined the plasticization effect of the system.

As a general evaluation all experiments were developed in the internal mixing at 9 minutes giving that this time provides us enough information about the plasticization, mixing and degradation behavior of the material.

- Tensile test, where the effectiveness of the plasticizer in the polymer was determined by measuring mainly the elastic modulus and the elongation at break.
- Differential Scanning Calorimetry (DSC), where glass transition temperature, crystallinity, melting point and crystallization temperature were measured.
- The morphology of PHB and its blends can be analyzed using microscopic methods like polarization optical microscopy POM.

KNEADING OR INTERNAL MIXING PROCESS

Internal mixing process is used to study the mixing process among species by considering the time dependence of the torque. The internal mixer machine consists of twin rotor mixers which are intermeshing and counter-rotating.

- Model device: Kneader Brabender 2100
- Load capacity: $V = 50 \text{ cm}^3$
- Maximum thermal load capacity = 400°C
- Maximum and torque: speed 100 RPM, torque 100 Nm
- Temperature: 165°C
- Screw speed: 48 RPM
- Mixing time: 30 minutes

Samples were prepared following the next conditions: for citric acid esters the concentrations in weight according to PHB were 20, 15, and 10%. Initially it was intended to prepare samples at higher concentrations, e.g. 40%, but exudation in samples was presented.

For all vegetable-oils-plasticizers the concentrations were prepared at 20, 15, 10, and 5%.

The materials used through all the experiments are the PHB as-received and the citric acid esters (commercially available); oils commercially available.

Table 1

Conditions for the preparation of samples PHB/plasticizers

Concentration plasticizer (%)	PHB Weight (g)	Citric Acid Esters (g)	Sample total weight (g)
20	40	10	50
15	42.5	7.5	50
10	45	5	50
0	50	0	50

Concentration plasticizers (%)	PHB content (g)	Vegetable oils Content (g)	Sample total weight (g)
20	40	10	50
15	42.5	7.5	50
10	45	5	50
5	47.5	2.5	50
0	50	0	50

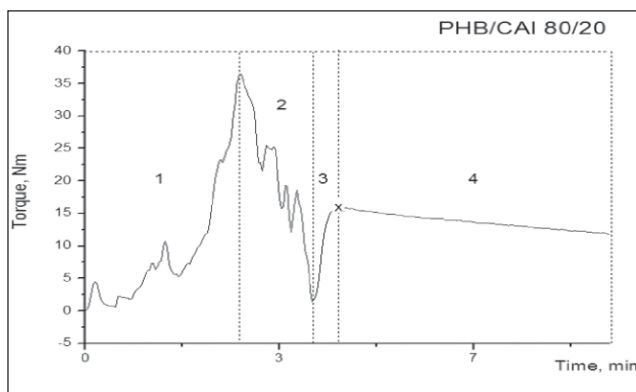


Figure 6. Kneading process of PHB/CAE'S.

In Figure 6 a typical diagram of a kneading process with citric acid esters is shown where:

1. Filling of PHB pure
2. Addition of plasticizer
3. Plasticization process and plasticization peak x – chamber closed
4. Mixing and thermal and mechanical degradation of the material

Addition of vegetable oils as plasticizer

A characteristic curve explaining the kneading process can be seen in Figure 7:

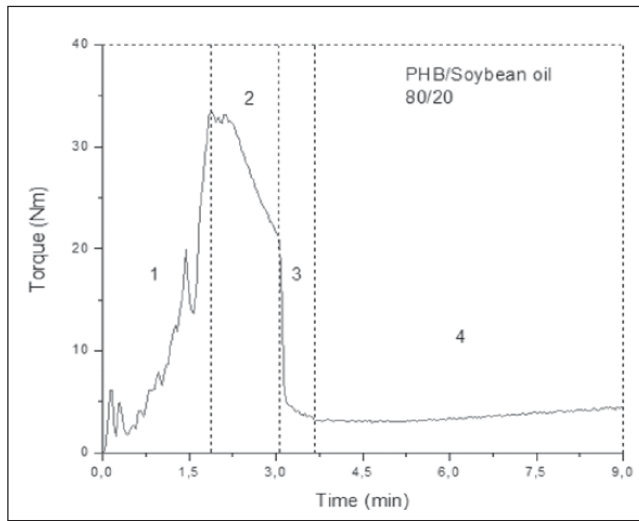


Figure 7. Kneading process of PHB/oils.

Figure 7 represents a standard curve for plasticization of PHB/oils, where:

1. Filling of the chamber with pure PHB.
2. Mixing time of PHB with chamber closed.
3. Opening of the chamber for addition of plasticizer –plasticizer addition.
x –chamber closed
4. Plasticization process, slight increment of the torque after 9 minutes.

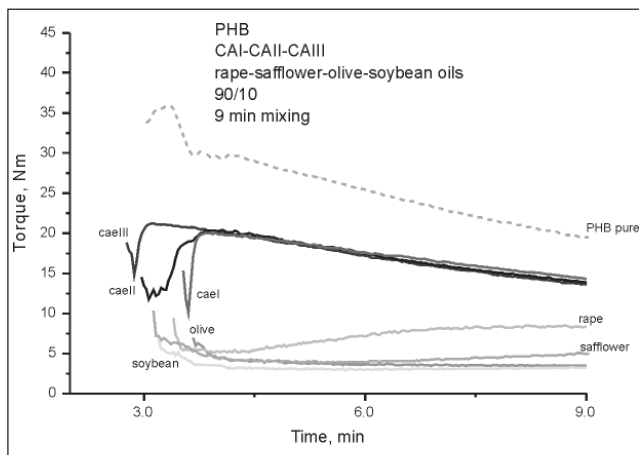


Figure 8. Plasticization process in the internal Mixing machine for PHB/CAE's and PHB/oils at 90/10.

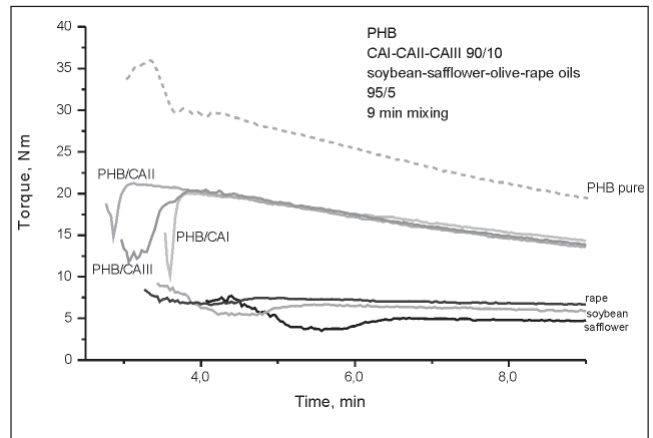


Figure 9. Plasticization process in the internal Mixing machine for PHB/CAE's and PHB/oils at 95/5.

Summary to Analysis of the plasticization process depending on type and ratio of plasticizers: Natural oils

- The only important result after 9 minutes of mixing time is the obtained with samples at 95/5 ratio. They presented a slight increase in torque after the filling process meaning that may be incorporation of particles into the PHB.
- Plasticization in oils may take place at longer mixing times as observed in figures 9 and 8. Rapeseed oil at ratio 80/20 and 90/10 and at ratio 90/10 for safflower oil showed an increase in torque after 9 minutes of mixing time, which mean that if the time of mixing is increased there could be a better plasticization of the material
- Olive oil did not take part in the plasticization process of PHB at any of the concentrations analyzed.
- In general the oils analyzed in this experiment do not show a good compatibility with the polymer matrix; this may be caused probably by the low molecular polarization effect offered by the natural oils, instead they tend to act as lubricants in the rotors of the mixers.
- When plasticization in oils is compared with the plasticization process realized by citric acid esters at different concentrations, from figures 8 and 9, it is concluded that the CAE's provide a better plasticizer effect on the PHB, and the plasticization with oils as mentioned above could take place in more time that in the experiments (9 minutes), as seen in the increment in torque for all samples.

MECHANICAL TEST

- Tensile testing machine device: Zwick/Roll Z005
- Clamp distance: 100 mm
- Speed 50 mm/min
- Range for E-Modulus detection at elongation between 0.05% -0.25%,
- Speed 1 mm/min
- Preforce of 0.3 MPa
- Tensile testing bar Type A1
- DIN 53455

PHB and citric acids

In Figure 10 the results of the addition of 20% of citric acids in PHB are shown. It was expected an important reduction in the elasticity modulus and also an increase in the elongation at break of the material. The first was corroborated whereas the latter applied only to the sample with CAEI. When compared with pure PHB the elasticity modulus was reduced 54% whereas the strain at break was increased to 241% passing from 6.30% to 21.5% being this result the best among all the experiments realized.

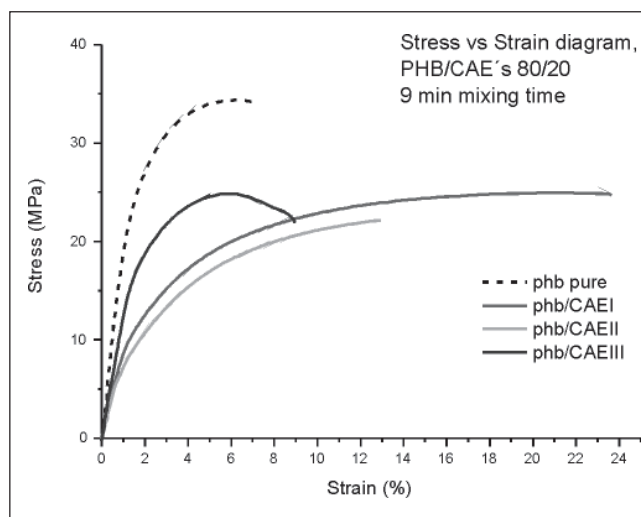


Figure 10. Stress vs. strain diagram PHB/CAE's 80/20.

The other two samples, CAEII and CAEIII, did not work out properly, especially the CAEIII which presented at a concentration of 10% a better performan-

ce. This may be explained by the segregation or saturation of the plasticizer when blended. CAEIII, when added at 15% of concentration, reduced the elasticity modulus in 24% but it only increased the strain at break in 6.4%. The same conclusion applies for CAEII. This plasticizer reduced significantly the elasticity modulus proportionally to the amount added into the polymer, but the strain at break did not improve when a concentration of 20% was used, meaning that a saturation point is found just around at 15% of concentration.

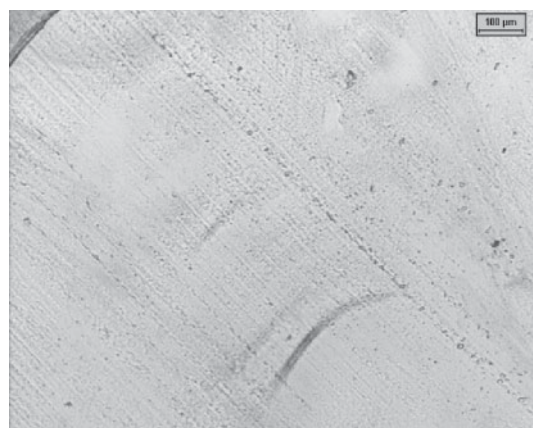


Figure 11. PHB/CAEI 80/20, 9 min mixing. Well dispersed blend with knife marks from the cutting process. POM 5X.

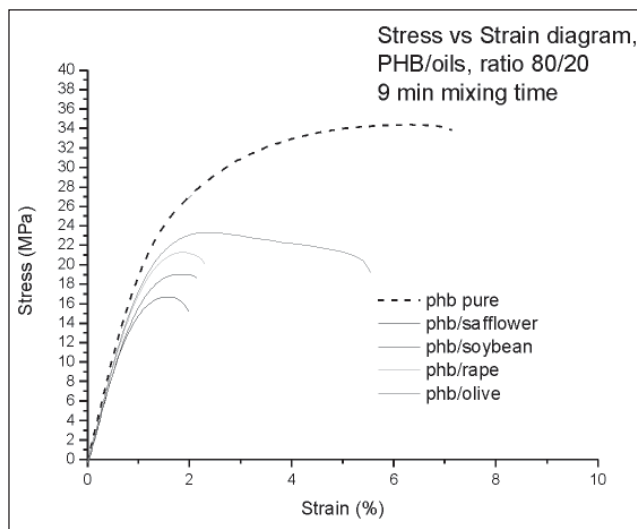


Figure 12. Stress vs. strain diagram PHB/oils 80/20.

Samples of PHB/oils ratio 80/20 are shown in Figure 12; here the incompatibility of PHB with oils is presented with a decrease in the tensile properties when

compared with the curve of pure PHB (black dash line). The material obtained here is completely brittle and fragile indicating that these plasticizers at this specific ratio were not effective for PHB as confirmed by the results of the internal mixing in which the chamber was completely saturated, meaning that there was no incorporation of oil particles into the polymer matrix. At this ratio also it is expected that oils behave more like a strong lubricant in the mixing device (figures 13 and 14).

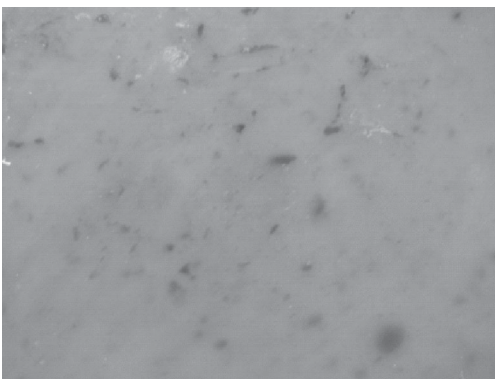


Figure 13. PHB/olive 80/20. Surface showing encapsulated oil which comes from saturation. Obviously mechanical properties have been affected. Digital camera.

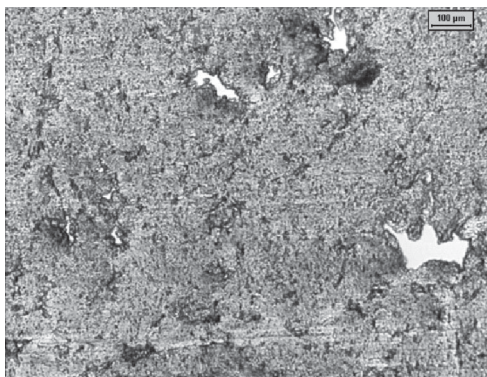


Figure 14. PHB/safflower at 80/20 ratio. System poorly dispersed due to incompatibilities. Holes caused by saturation or contamination of the polymeric matrix. POM 5X.

When oils are mixed in concentration of 5% better results are observed and it may indicate a plasticization process in the end up product. As seen in Figure 15 the resulting material combines good mechanical properties with high tensile modulus, a clear elastic and plastic

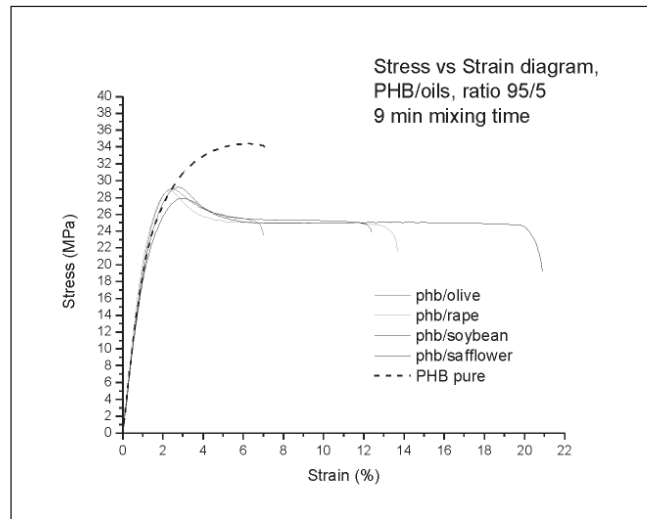


Figure 15. Stress vs. strain diagram PHB/CAE's 95/5.

region and a high yield strength point ending up with an increment in the strain at break when compared with samples at 20% weight concentration and compared also with the pure material itself. For all samples, the elasticity modulus was reduced just slightly, being safflower (9% less modulus than the pure material) the best product, whereas rapeseed, soybean and olive decreased the modulus just in some fraction. When strain at break is observed, it is found that safflower improved in rising it to 171%. This result is comparable with data from CAEI. This behavior is corroborated with the results of the internal mixing which exhibited at this ratio a plasticization effect (slight increase of torque after filling the chamber). It is possible conclude that the concentration of 5% is the only possible combination acceptable in this report, giving that at



Figure 16. PHB/safflower 95/5. A well dispersed system is observed. POM 5X.

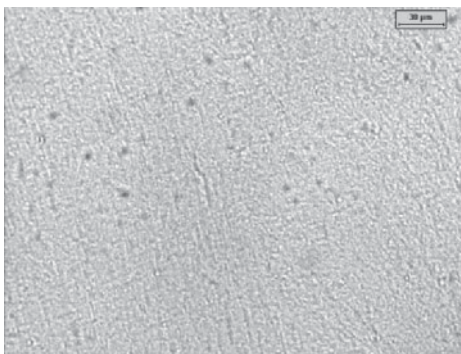


Figure 17. PHB/soybean 95/5. POM 20X.

10% amount of plasticizer the strain at break did not improve with any of the oils evaluated when compared with the pure PHB. The elasticity modulus at this concentration was reduced only some points, implying that the rigidity and specifically the brittleness of the material were not reduced significantly. Data presented in this example also demonstrate once more that the olive oil is not acting as a plasticizer in any of the experiments. Here this material did not improve the strain at break nor the elasticity modulus was reduced when compared with the pure material and it also contained a high elasticity modulus resulting in a very brittle and fragile material. This was also demonstrated in the internal mixing process where no torque-rise was observed; for that reason, it was excluded from the analysis in that chapter. In general, the use of oils as plasticizers deserves further investigation, specially in

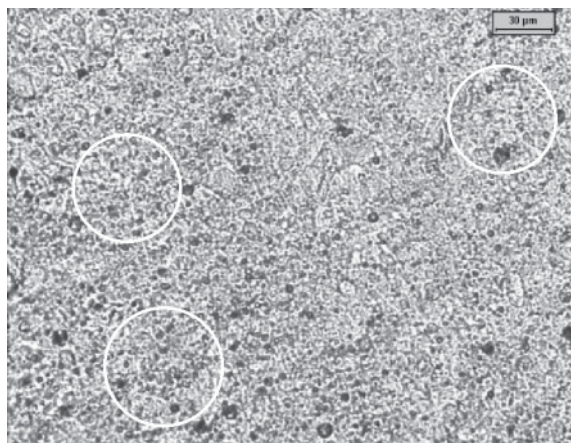


Figure 18. PHB/olive 95/5 poorly dispersed olive oil, confirming the total incompatibility of this material with PHB. Circles correspond to oil droplets encapsulated in the PHB matrix. POM 20X.

finding a right saturation point which probably is located between 10% and 5% of concentration. This also give us notice about the breaking point of the oils acting as plasticizer and turning it into lubricant which ruined up the plasticization process in the internal mixer.

In Figure 19 the behavior of the additives according to elastic modulus is shown. From these, it is determined that both types of plasticizers, CAE´s and oils, reduced the elastic modulus when concentration of plasticizer is augmented if compared with pure PHB. An important reduction of the E modulus is observed in the blends PHB/CAE´s, especially for CAEI and CAEII which diminished this variable in 54% and 61% respectively, indicating that the material behaves according to its stress-strain behavior like a soft-ductile material due to its smaller E modulus and smaller tensile strength at break. PHB/oils present a small reduction in E modulus, just 17% for PHB/safflower at 90/10 ratio, and approximately a decrease of 12% at 80/20 ratio for the other oils. At 5% concentration soybean and rapeseed oil do not alter the E modulus of the pure material, but safflower provides a 10% less brittle material.

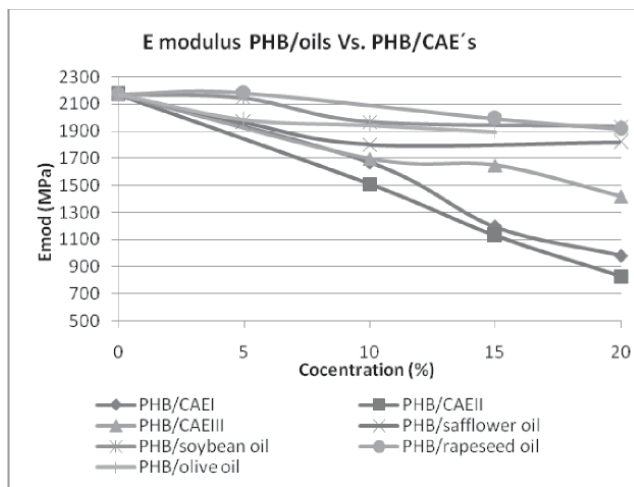


Figure 19. E modulus vs. concentration – oils and CAE´s.

From the strain at break curves in CAE´s it is determined that sample blended with CAEI displayed an expected tendency increasing the percentage of elongation when the concentration of plasticizer was also increased; in this case, the highest strain at break was observed at a content of 20% with an increment of

241% when compared with PHB alone. CAEII and CAEIII do not follow a clear tendency when content of plasticizer is rising; this is probably because the saturation point or plateau for both additives is observable at 10% concentration. Further addition results, for either CAEII or CAEIII, in a reduction of the strain at break.

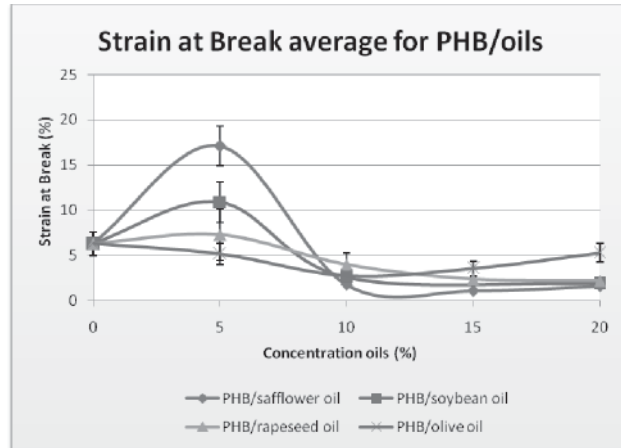


Figure 20. Strain at break vs. concentration in oils.

The results of strain at break for oils are clear and confirm the data evaluated in the internal mixing process. Figure 20 shows that the highest level of strain at break reached was obtained when oils were added at a ratio 95/5. The blending PHB/safflower oil was the best combination, presenting an increment of approximately 171% when compared with the pure PHB. In that tendency PHB/soybean increased 73% the elongation at break whereas PHB/rapeseed showed an improvement of just 15%. PHB/Olive oil blends, as observed in all tests, is completely incompatible with PHB and do not present any result which could be comparable with the other blends. Voids are observed in this system (Figure 18).

Summary to Mechanical test

The brittleness of PHB could be overcome by blending with CAE's as shown in Figure 12. From these, the CAEI at ratio 80/20 contain in these report the best results. When compared with pure PHB, the elasticity modulus was reduced 54% whereas the strain at break was increased to 241% reaching at the end a strain at

break of 21.5%, being this result the best among all the experiments realized. CAEIII work out better at lower concentrations, e.g. 90/10, with 98% improvement in the elongation at break.

When oils are mixed in concentration of 5%, better results are observed and they may indicate a plasticization process in the blended system. As seen in Figure 15, the resulting material combines good mechanical properties with high tensile modulus, a clear elastic and plastic region and a high yield strength point. Safflower came out with an improvement in the strain at break raising it to 171%, almost comparable with the best result obtained with CAEI. This behavior is corroborated with the results of the internal mixing process. The ratio 95/5 is the only possible combination in this report, in the case of oils.

As a general point, the use of oils as plasticizers deserves further investigation, specially in finding the right saturation point which probably is located between 10 and 5% of concentration.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC is a commonly used method for the thermal analysis of polymers used to measure the heat capacity of a sample as a function of temperature (3). DSC determines the quantity of heat that is either absorbed or released by a sample that undergoes a physical or chemical change which alters the internal energy known as enthalpy. H is defined as:

$$\Delta H = \int C_p \cdot dT$$

Eq. 1 Enthalpy.

where C_p is the quantity of energy needed to raise the temperature of 1 g of material by 1 °C at constant pressure, this is known as specific heat capacity; and dT is the variation in temperature.

DSC device: Mettler Toledo 820, heat flux type
Method: T min -50°C Tmax = 200°C HR=10°C/min, CR=10°C/min, purge element: N₂=80ml/min

Conditions and program for PHB/plasticizer system:

- **First heating rate:** The samples (between 5 -15 mg) when encapsulated and introduced into the machine are heated from 25 to 200°C at a heating rate of 10°C/min, once at 200°C. There is a holding time of 2 minutes.
- **First cooling rate:** after 2 minutes at 200°C and a cooling rate of 10°C/min, samples reach a temperature of -100°C. There is a holding time of 2 minutes at -100°C.
- **Second heating rate:** after a holding time at -100°C = 2 min, increase with a rate of 10°C/min to a maximum temperature of 200°C. Holding time at 200°C = 2.
- **Second cooling rate:** at the same rate (10°C/min) decrease temperature to 25°C to finish the experiment.

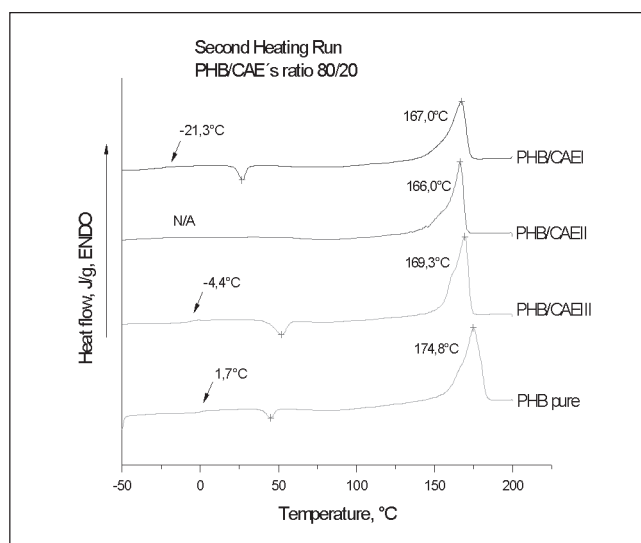


Figure 21. Second heating cycle PHB/CAE 's 80/20.

From Figure 21, it is seen that the maximum melting temperature slightly decreases in all blends when compared with the PHB alone. The most efficient effect is detected in the blend PHB/CAEII at ratio 80/20 with a final T_m of 166,0°C; this is attributed to the effect of disordering of the crystalline part of PHB due to the presence of the plasticizers in the polymer phase. In other words, a somewhat less ordered but more homogeneous crystalline phase is formed.

Curves show also a distinct exothermic peak of cold crystallization of PHB in the temperature range 20°C – 50°C for all concentrations. This phenomenon

highlight the crystallization of the part of PHB which did not have time to crystallize upon rapid cooling. The only system which did not present such a behavior was the PHB/CAEII, indicating probably that a fully equilibrium crystalline phase arises here.

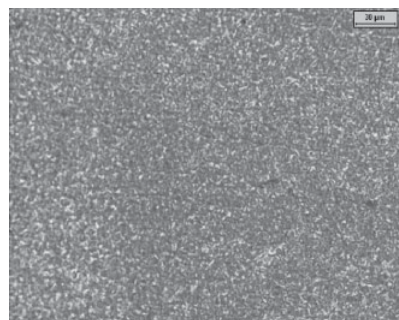


Figure 22 PHB/CAEII 90/10. From here it is assumed that the size of spherulites and crystallization process is homogenous. POM 20X.

For all systems (CAE 's at different concentration), one glass transition temperature (T_g) is registered which indicate a complete compatibility of the plasticizer with PHB; as expected, the plasticizers investigated decreased the T_g with respect to that of the original material. This is explained by the weakened of the intermacromolecular interaction in the amorphous part of PHB and the increase in the free volume. The lowest T_g is observed in the PHB/CAEI-80/20 curve with a T_g of -21,3 °C.

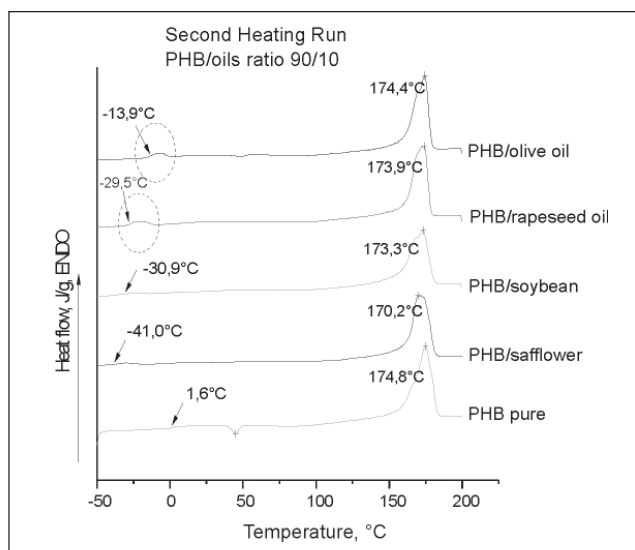


Figure 23. Second heating run PHB/oils 90/10.

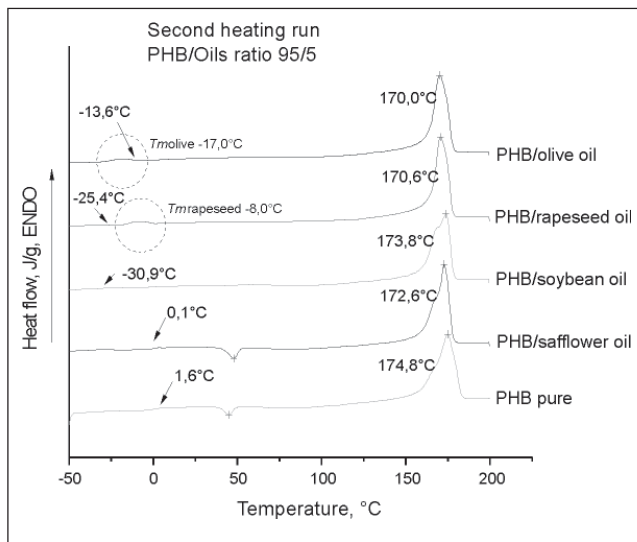


Figure 24. Second heating run PHB/oils 95/5.

When T_m is analyzed from figures 23 and 24, the maximum melting temperature decreases a few grades in all blends when compared with the original value of the pure material. The highest reduction is detected in the blends PHB/safflower at ratio 90/10 and PHB/olive at ratio 95/5 reaching a final T_m of $-170,0^\circ\text{C}$ (Figure 24). It is seen also that a series of dual peaks or small shoulders are formed specially in the melting process of PHB/oils at ratio 90/10 (soybean, rapeseed and oil). These results from two different crystal modifications in the pure material making the quantitative interpretation of their heating curves difficult. It seems reasonable to conclude in these cases that the PHB might have been contaminated by residual particles of oils, clearly explained by a saturation of

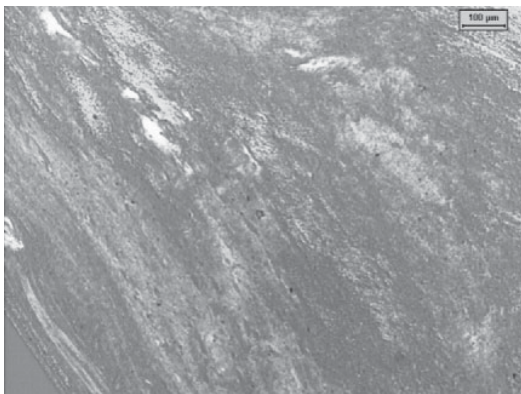


Figure 25. Poorly dispersed sample containing soybean at 15%. POM 5X.

the content of plasticizer at 90/10 ratio. At lower concentrations, e.g. 95/5, this behavior was observed by the sample with soybean oil.

In figures 23 and 24, aside from the dominant melting peak of the PHB (approx. 170°C), the DSC analysis displays small melting peaks highlighted by dashed circles that may represent melting temperatures of the oils described. This is clearly related to the little structural similarity of the two semicrystalline materials. Theoretical values for melting temperatures of olive and rapeseed oil are pointed at -6°C and -10°C respectively (39). In general for PHB/oils at 95/5, the temperature range of the melting process becomes narrower; this means that, in presence of plasticizers, a somewhat less ordered but more homogeneous crystalline phase is formed.

Blend PHB/safflower at 95/5 ratio in Figure 24 shows also a distinct exothermic peak of cold crystallization of PHB in the temperature range $25^\circ\text{C} - 50^\circ\text{C}$. As mentioned previously, this phenomenon highlights the crystallization of the part of PHB which did not have time to crystallize upon rapid cooling; the other blends without the cold crystallization peak may indicate that a fully equilibrium crystalline phase arises there.

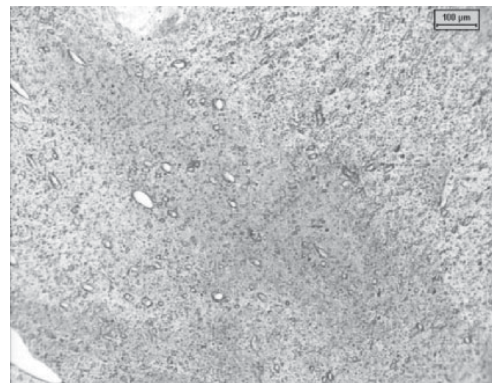


Figure 26. PHB/soybean 85/15 containing voids. POM 5X.

For each system analyzed (oils at different concentration), one glass transition temperature (T_g) is registered. As expected, the plasticizers investigated decreased the T_g with respect to that of the original material; nevertheless the T_g measured in oils at 10% concentrations was registered by the machine assuming this temperature from the small melting peaks of oils.

From the first cooling run all, PHB/oils blends show a crystallization peak occurring at higher temperatures when compared with the crystallization of the pure material this may explain the influence of the oils on the processing of PHB. Oils or some contaminated fractions of PHB could act as a nucleating agent and displace the crystallization curve to the right as obtained in curves, from here the nucleation and growth rates of spherulites are faster than the crystallization process in the pure PHB.

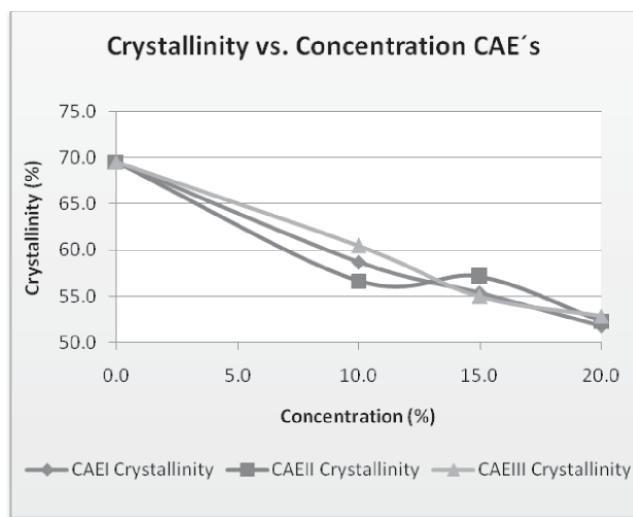


Figure 27. Crystallinity by DSC vs. Concentration CAE's.

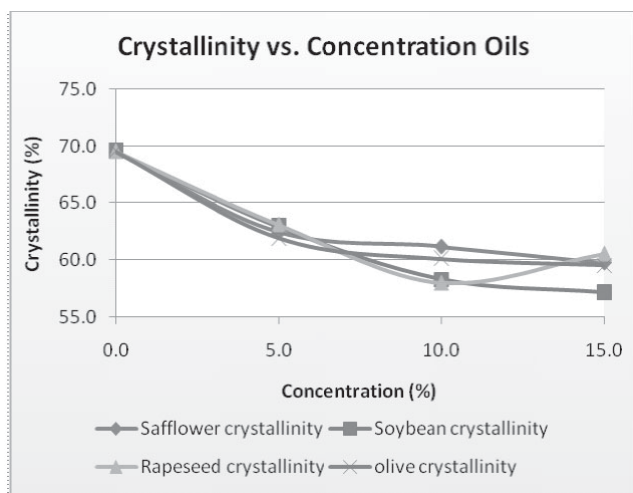


Figure 28. Crystallinity by DSC vs. Concentration oils.

When crystallization is plotted against content of plasticizer in figures 27 and 28, all plasticizers, as expected, caused a considerable decrease in crystallinity when the concentration is augmented due to the role played by a foreign substance present in a crystallizing polymer which generates a disorganizing effect in the matrix of PHB. Better results in reduction of crystallinity were obtained by the systems PHB/CAE's which reached at 20% concentration a crystallization value close to 52% when the original crystallinity of the PHB was closed to 70%. This can be explained by the higher degree of compatibility showed by CAE's when compared with the vegetable oils which were assumed as real plasticizers.

CONCLUSIONS

Plasticization in the internal mixing device depends on time of internal mixing and on the amount and kind of plasticizer added. It was determined that plasticization induced by CAE's and oils at low contents occurs at different mixing times. When the concentration of these additives is lowered the plasticization process takes place at shorter times; compatible additives, such as CAE's, obviously contribute to the process.

The temperature profile decreased during the mixing process with all plasticizers at any concentration; this mean that the small processability window recorded in literature for PHB is widened here, avoiding thermal degradation of the material.

When oils are processed in the mixer at high concentrations they perform more like a lubricant than a real plasticizer: shear rate is lowered making dispersion and addition of particles in the polymer matrix a difficult task; this is registered in low torque. At high contents also, e.g. 10% and 20%, plasticization may take place at longer mixing times specifically rapeseed oil at ratio 80/20 and 90/10 and safflower at ratio 90/10. This could be attributed to the secondary lubricating effect of oils inside the machine. An important effect is the one obtained with samples at 95/5 ratio. They presented a slight increase in torque after the filling process meaning that there exists incorporation of particles into the PHB. In general the oils analyzed in this report do not show a good compatibility with the polymer matrix, this may be caused probably by low polarization effect in the intermacromolecular region.

It may be assumed that CAE's have a real effect in PHB giving that in the internal mixing process there was a clear increase in torque after the addition of them, indicating a complete incorporation of the particles into the polymer. The plasticization effect was clearer for those systems mixed at 90/10 ratio; however, for samples with higher plasticizer ratios, 85/15 and 80/20, the reduction of the maximum temperature profile was important facilitating the further processability of the material without thermal degradation.

The brittleness of PHB has been improved by blending with CAE's; from those systems the CAEI at ratio 80/20 displayed in this report the best results. When compared with pure PHB the elasticity modulus was reduced 54%, whereas the strain at break was increased to 241% reaching at the end a strain at break of 21.5%, being this result the best among all the plasticizers utilized. On the other hand, only PHB/oils systems mixed at 5% concentration yield good results; it may indicate a plasticization process in the end-product as recorded also in the internal mixing process. The resulting material combines good mechanical properties with high tensile modulus, clear elastic and plastic region and a high yield strength point. Safflower gave an improvement in the strain at break raising it to 171%.

For oils the ratio 95/5 is the only possible combination acceptable in this report. According to data from the internal mixing, tensile, and DSC tests, olive oil is not acting as plasticizer in any of the experiments.

As a general point the use of oils as plasticizers deserves further investigation specially in finding a right saturation point which probably is located between 10 and 5% of concentration; it is also recommended make the internal mixing process at longer times to corroborate or not if the plasticization process will take part at times longer than 9 minutes of mixing.

It could be expected that the plasticizers causing a sharp decrease in T_g in PHB would considerably increase the elongation at break of the polymer. For the most of the plasticizers studied, this regularity was not observed in practice (as shown in figures representing the mechanical properties and T_g); the experimental data available are not sufficient for presenting an explanation for this factor. The most efficient decrease in T_g and T_m was observed with the addition of CAEI at 20% content. Systems blended with CAE's and oils

influenced the crystallization temperature, oils moved it to higher values in temperature when compared with the data from PHB pure. This may be explained by the fact that oils or some contaminated fractions of PHB could act as a nucleating agent and displace the crystallization curve; besides, systems blended with CAE's moved the crystallization process to lower temperatures which may be explained by the performed nucleation of the additive which probably reduces the mobility of the PHB, retarding the lamella formation. All plasticizers analyzed caused a considerable decrease in crystallinity when the concentration is augmented due to the role played by a foreign substance present in a crystallizing. Better results in reduction of crystallinity were obtained by the systems PHB/CAE's which reached at 80/20 ratio a crystallization value close to 52% when the original crystallinity of the PHB was recorded at 70%.

From data obtained in this report, it is necessary to evaluate and state some conclusions about the functionality of the plasticizers evaluated, in this case CAE's and vegetable oils. The functionality of the polymer/plasticizer system depends on the low molecular weight and the number of polar groups in the plasticizer. From here, it is concluded that there exist a polar compatibility that ranged from slightly to strongly polar interaction. CAE's present a strong compatibility with the polar polymer (ester groups) and a non polar functionality for internal lubrication (hydrocarbons). The polar portion of the plasticizer provides the attractive force necessary to attach to the polymer chain, so in that way the plasticizer is attached to the polymer in the points of polar attraction, whereas the non polar or hydrocarbon region which is not attractive act as a lubricant between polymer chains. In the case of oils the lacking of strong polar groups, e.g. esters or aromatic groups, induces in the polymer mostly a lubricant effect between the macromolecules, especially at high content of plasticizer, due to the large hydrocarbon branches presented in the fatty acid molecules which result in a poorly dispersed system when blended with the polymer, affecting the mechanical and thermal properties. The non polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group; this may explain the acceptable and poor behavior of the safflower and olive oils as plasticizers in PHB. It is expected that the acid functional group

of safflower oil (linoleic acid for safflower, oleic and palmitic acid for olive) dominates and gives the whole molecule a more polar character than the other oils, whereas the longer non polar hydrocarbon chains give the molecule a non polar character. This characteristic is clear for olive, and rapeseed oils.

OUTLOOK AND RECOMMENDATIONS

With base on the procedures realized and results obtained, it is recommended for further investigation that:

- Verify if the plasticizers migrate from the polymer matrix, especially for CAE's at all the concentrations and oils at 5% content. The same experiments have to be done to the samples with a difference of at least 6 months to check if the mechanical and thermal properties are affected by time between experiments. It is expected that, if the plasticizers migrate or volatilized from PHB, the properties would be diminished drastically; that is recorded mainly by a higher brittleness, higher crystallinity and less elongation at break.
- Synergies are also interesting to investigate, for example, analyzing the behavior of systems with synergies between CAE's and oils, or between these plasticizers and nucleating agents which could improve the mechanical properties via reduction of crystallinity.
- It is important determine the DSC curves for oils alone, and compare them with the results obtained in blends at ratios 90/10 and 95/5 because the T_g recorded could be understood as the melting temperature corresponding to the oils themselves and not to the T_g corresponding to the final blended product.
- From the results of the internal mixing process it is suggested realize the mixing process for the samples blended with oils at higher mixing times. This could be done by try-error experiments with a starting mixing time of 30 minutes to determine if there exists a possible plasticization process in this range of time.
- Use of epoxidized oils to improve the reactivity of the plasticizers via increasing of the polarity, as shown in molecules. A few papers have established

that epoxidized soybean oil has brought better results when compared with the non epoxidized molecule; this is mainly achieved by the cyclic ether with only three ring atoms. This ring approximately is an equilateral triangle, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers; consequently this will provide a better compatibility of the plasticizer to the macromolecular structure of the polymer matrix.

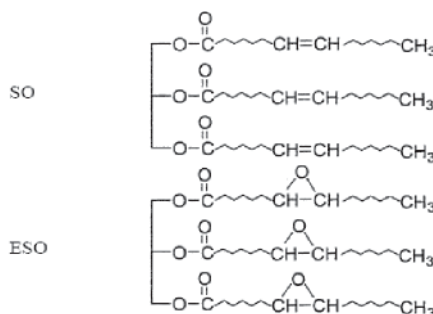


Figure 70. Soybean and epoxidized soybean (21).

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