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**“A new biobased plasticizer for poly (vinyl chloride), PVC based on epoxidized  
cottonseed oil (ECSO)”**

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**Abstract**

The use of epoxidized cottonseed oil (ECSO) as plasticizer for poly(vinyl chloride), PVC was studied. The plasticizer content was set to 70 phr and the optimum isothermal curing conditions were studied in the temperature range comprised between 160 °C and 220 °C with varying curing times in the 7.5 - 17.5 min range. The influence of the curing conditions on overall performance of cured plastisols was followed by the evolution of mechanical properties (tensile tests with measurements of tensile strength, elongation at break and modulus), change in colour, surface changes of fractured samples by scanning electron microscopy (SEM), thermal transitions by differential scanning calorimetry (DSC) and migration in *n*-hexane. The optimum mechanical features of cured plastisols are obtained for curing temperatures in the 190-220 °C range. For these curing conditions, fractography analysis by SEM gives evidences of full curing process as no PVC particles and free plasticizer can be found.

**Keywords:** epoxidized cottonseed oil (ECISO); poly (vinyl chloride), PVC; plastisols; mechanical properties; isothermal curing.

## **1. - Introduction.**

Poly(vinyl chloride), PVC is one of the most widely used commodity plastics<sup>1</sup>. It can be manufactured by conventional techniques such as rotational molding, extrusion, injection molding, blow molding and calendaring, among others, depending on the final product<sup>2,3</sup>. PVC can be easily plasticized to give flexible materials (P-PVC) with tailored properties which find a wide variety of applications such as blood bags, films and coatings, flexible toys, insulation for electrical wires and soles due to the high versatility, easy processing and low cost<sup>4-8</sup>. Plastisols, or PVC pastes, are obtained by mixing a PVC resin with a liquid plasticizer to form a dispersion of resin particles in plasticizer. With heating, plasticizer diffuses into the resin particle solvating the non-crystalline parts of the polymer chain and causing the resin particles to swell. With further heating the plasticizer can solvate (fuse) the crystalline sections of the polymer, some of which effectively crosslink the resin, allowing polymer molecules originally found in different resin particles to interact. This paste can be converted into a flexible solid material by a curing process which involves heating the paste to a certain temperature for a given time<sup>9</sup>. Vinyl plastisols are characterized by high wear and corrosion resistance, as well as excellent electric insulation. By varying the plasticizer content it is possible to tailor the final properties of the cured plastisols<sup>10</sup>.

Phthalates, citrates, adipates and carboxylates, among others, have been traditionally used as PVC plasticizers being phthalates the main group due to low cost and excellent overall properties<sup>11</sup>. Nevertheless, the use of phthalate-based plasticizers is being reconsidered due to toxicity problems and plasticizer migration<sup>5,12</sup>. For this

reason, new environmentally friendly plasticizers are being demanded by the PVC industry to fulfil the increasingly rigorous requirements of some industrial sectors. Epoxidized vegetable oils offer interesting possibilities in PVC plasticization. Their use as main plasticizer or, more often as secondary plasticizers is continually increasing; it is possible to find recent works based on the use of epoxidized vegetable oils derived from linseed oil, castor oil, soybean oil, sunflower oil, rubber seed oil, etc. as plasticizers for vinyl plastisols formulations<sup>13-15</sup>.

In this study epoxidized cotton seed oil is used due to the surplus produced in the industry and also because it is a by-product of the cotton industry, with about 5.12 million tons production in 2014/15<sup>16</sup> being China and India the major producers with 1.396 and 1.320 million tons respectively. Other reasons for its use is the relatively high oxirane oxygen index achieved after epoxidation process (5.32%). This value is slightly lower than other readily available epoxidized vegetable oil such as epoxidized soybean oil (ESBO). ESBO is widely used as secondary plasticizer for PVC, thermal stabilizer for plastic formulations and base material for polymer synthesis. For this reason, as epoxidized cottonseed oil (ECSO) has a similar oxirane oxygen index to that of an epoxidized soybean oil, it is reasonable to expect similar performance although their respective lipid profiles and other contained chemical compounds are different.

The main concern about the use of phthalate-based plasticizers such as DBP (di-n-butyl phthalate), DIBP (diisobutyl phthalate), BBP (butyl benzyl phthalate), DEHP (bis(2-ethylhexyl) phthalate) and DIOP (diisooctyl phthalate) is their volatility and also their migration promoted by their relatively low molecular weight<sup>17-20</sup> which is also responsible for good mixing with PVC particles<sup>21</sup>. Typical molecular weight of phthalate-based plasticizers is lower than 400 g mol<sup>-1</sup> as it is the case of bis(2-ethylhexyl) phthalate with a molecular weight of 390.56 g mol<sup>-1</sup> or di-n-butyl phthalate

with a molecular weight of  $278.3 \text{ g mol}^{-1}$ . On the other hand, the typical molecular weight of epoxidized vegetable oils is around  $900\text{-}950 \text{ g mol}^{-1}$ , which has a positive effect on migration restriction. Today, some high molecular weight phthalate-based plasticizers such as di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP) and di-2-propylheptylphthalate (DPHP) are permitted as common plasticizers in such applications that require low migration<sup>8,22,23</sup>.

The final mechanical features of the cured plastisols will depend on the curing cycle in terms of temperature and time. After mixing PVC resin with the plasticizer, the gelation process begins. This process can be divided into three different stages. Initially, the plastisol consists of PVC resin fine particles dispersed in a liquid plasticizer. With heating, the first stage in the gelation process begins. Plasticizer diffuses into the resin particles solvating the non-crystalline parts of the polymer, swelling the particles and causing a dramatic rise in the PVC paste viscosity. Plasticizer interacts with the somewhat polar PVC resin through electrostatic interactions including dipole-dipole and van der Waals forces<sup>24</sup>. This stage continues until all of the plasticizer has been absorbed into the resin particles<sup>25</sup>. With continued heating, the second stage of the plastisol gelation/fusion process begins. At these higher temperatures plasticizer can solvate (fuse or melt) the crystalline parts of the PVC resin causing the PVC paste viscosity to drop and allowing polymer molecules to flow more freely and interact with polymer molecules from other resin particles. Upon cooling, the final stage in the gelation/fusion process begins. Crystallites form again effectively crosslinking polymer molecules. Physical entanglement of the processed flexible PVC polymer chains as well as crystalline crosslinks between polymer molecules provides its mechanical strength to the finished product. Plasticizer solvates the non-crystalline parts of the PVC polymer giving the finished product its particular flexibility<sup>22,26</sup>.

In commercial practice, P-PVC curing conditions affect efficient production and finished product properties. A low processing temperature profile leads to under-curing, which leads to poor mechanical performance. On the other hand, a high temperature profile promotes PVC degradation and, subsequently, a remarkable loss in mechanical properties<sup>27</sup>.

This research work is a preliminary study about the possibilities of epoxidized cottonseed oil (ECSO) as biobased and environmentally friendly plasticizer for PVC plastisol formulations with potential use as substitute for conventional phthalates. PVC plastisols with constant plasticizer content (70 phr) were subjected to different curing cycles in terms of temperature and time; the effect of the curing parameters on mechanical performance, change in color, thermal transitions, and migration of PVC plastisols was evaluated to assess optimum curing conditions for this system.

## **2.- Experimental.**

### **2.1.- Materials.**

PVC plastisols were obtained with a commercial suspension PVC (Lacovyl PB 1172 H) with K-value 67, supplied by Atofina (Atofina UK, Ltd, Midlands, United Kingdom). The base vegetable oil for plasticizer synthesis was cottonseed oil supplied by Sigma Aldrich (Sigma Aldrich España, Madrid, Spain). This vegetable oil is characterized by an iodine value in the 109-120 range and a density of 0.92 g cm<sup>-3</sup> which makes it suitable for epoxidation. In a previous research work the influence of different epoxidation process parameters were optimized<sup>28</sup>.

## ***2.2.- Plastisol preparation.***

PVC pastes with constant plasticizer content (70 parts per hundred parts of resin) were prepared in a mixing bowl of 1500 cm<sup>3</sup> by mixing the appropriate amounts of each component (85.72 gr PVC and 60 gr ECSO) at 23 °C for 10 min at 200 rpm in a rotational mixer KAPL mod. 5KPMS (KAPL, Michigan, USA). Once homogeneous pastes were obtained, pastes were subjected to degassing in the same container for 1 h in a vacuum chamber MCP 00/LC (HEK-GmbH, Lubeck, Germany) to remove all entrapped air bubbles. After that, the liquid plastisols were placed into an aluminum mold with rectangular shape to obtain sheets sizing 190 x 135 x 4 mm<sup>3</sup>. As other authors have reported previously, an aluminum mold with a low thickness (less than 1 mm) has been used due to low heat dissipation<sup>27</sup>. The curing process was carried out at different temperatures comprised in the 160 – 220 °C range with varying times in the 7.5-17.5 min in an air circulating oven mod. Selecta 2001245 (JP Selecta S.A., Barcelona, Spain). Standard samples for the different tests were obtained with a hot press mod. MEGA KCK-15A (Melchor Gabilondo SA, Vizcaya, Spain) using an appropriate die.

## ***2.3.- Mechanical characterization of cured PVC plastisols.***

Mechanical properties of cured PVC plastisols subjected to different curing cycles were obtained in a universal test machine Ibertest ELIB 30 (Ibertest S.A.E., Madrid, Spain) following the guidelines of the ISO 527. The size of the samples for tensile tests was obtained as recommended by the previous standard. The specific dimensions used to calculate the cross section of each sample were 10 mm of width and 4 mm of thickness  $\pm$  0,2 mm. Tensile tests were carried out at a crosshead speed of 20

mm min<sup>-1</sup> at 23 °C. Five different samples were tested and average values of tensile strength, elongation at break and modulus were calculated.

#### ***2.4.- Surface characterization by scanning electron microscopy (SEM).***

Before observation, the surface of fractured samples from the tensile test was subjected to a sputtering process in a Sputter Coater EMITECH mod. SC7620 (Quorum Technologies Ltd, East Sussex, UK) and subsequently, samples were observed in a scanning electron microscope FEI mod. PHENOM (FEI Company, Eindhoven, The Netherlands) at an accelerating voltage of 5 kV.

#### ***2.5.- Solvent extraction test.***

The solvent extraction test was carried out in *n*-hexane and the global migration was estimated by gravimetric measurements. Circular samples (25 mm diameter) were immersed in *n*-hexane and periodically removed to measure weight loss/gain. The solvent extraction test was carried out at different temperatures between 30 °C and 60 °C and the global migration was obtained for different migration times: 2, 4, 6 and 8 h.

#### ***2.6.- Thermal characterization of cured plastisols.***

Thermal characterization of cured plastisols was carried out by using differential scanning calorimetry (DSC) in a DSC 821e (Metler-Toledo S.A.E., Barcelona, Spain). Samples with an average weight of 6-7.5 mg were subjected to a heating program from -50 °C up to 60 °C in air atmosphere at a heating rate of 5 °C min<sup>-1</sup>.

#### ***2.7.- Measurement of colorimetric coordinates of cured plastisols.***

Color coordinates were measured on cured samples subjected to different curing conditions using a Hunter Mod. CFLX-DIF-2 colorimeter (Hunterlab, Murnau, Germany). This equipment provides different colour scales but the selected coordinates were (L\*a\*b\*). This colorimeter also provides spectral data from 400 to 700 nm so that it is useful for opaque and translucent materials as it is the case of plastisols cured in different conditions.

### **3.- Results and discussion.**

#### ***3.1.- Influence of curing time and isothermal curing temperature on mechanical properties of cured PVC plastisols.***

The curing cycle of a liquid plastisol is defined in terms of the isothermal curing temperature and the necessary time to reach optimum mechanical properties on cured plastisols. Fig. 1a shows the plot evolution of the tensile strength as a function of the curing time for different curing temperatures in the 160-220 °C range. The tensile strength of plastisols cured at the lowest considered temperature (160 °C) is lower than 3 MPa which is representative of very poor mechanical properties. The curing process has not been completed and that is why mechanical performance is very poor and the cured plastisol behaves as a wax. For this plastisol series it was impossible to test the material subjected to a curing time of 7.5 min as it collapses easily even with very low loads (typical of a waxy consistence). This behavior is typical of not fully cured plastisols. The plasticizer has promoted swelling of individual PVC particles but the temperature has not been high enough to completely melt the PVC<sup>27</sup>. All PVC plastisols, except the one cured at 220 °C, provide increasing tensile strength values as the curing time increases. Tensile strength values of about 11.6 MPa can be obtained with curing conditions of 205 °C and a curing time of 17.5 min. Plastisols cured at 220

°C show a different behavior as initially (for low curing times) the tensile strength increases as observed with lower curing temperatures; nevertheless, when a certain curing time is reached, we observe a clear decrease in tensile strength values. This is directly related to thermal degradation of the PVC and important plasticizer loss as a consequence of the exposure of a liquid PVC paste to high temperatures and long times. For this reason, the material becomes brittle and a slight decrease in tensile strength is observed. As it can be observed in Fig. 1a, it is possible to reach a particular tensile strength value by combining different curing temperatures and times; so that, even accounting standard deviations, plastisols cured at 205 °C for 15 min offer the same tensile strength than plastisols cured at 220 °C for 10 min. This could be interesting from industrial point of view as a reduction in the curing cycle could represent a reduction in manufacturing cycles; despite this, the use of high curing temperatures is dangerous as slight changes in the curing time could lead to a noticeable change in mechanical properties as observed in Fig. 1a. Nevertheless, as PVC is highly sensitive to thermal degradation and this phenomenon has a negative effect on mechanical performance, even more conservative curing conditions at 205 °C for 15 min could be considered as appropriate.

With regard to elongation at break (Fig. 1b) we observe an increase as both temperature and curing time increases. Again, the lowest elongation at break values are obtained for plastisols cured at 160 °C and this is representative for under-curing conditions and, consequently, the typical flexibility of well-cured plastisols is not achieved. Curing at 190 °C provides the highest slope in elongation at break; this increases by 625% with a change in curing time from 7.5 min to 12.5 min; after this remarkable increase, it remains almost constant with values between 130% and 140%. As indicated previously, the evolution of the elongation at break for plastisols cured at

220 °C offers two clear zones: for low curing times, we observe an increasing tendency up to curing times of about 12.5 min. Once this curing time is reached, a clear decrease in flexibility can be detected by a dramatic decrease in elongation at break values up to 30% (for a curing time of 17.5 min). As expected, the combination of high curing temperatures and long times define over-curing conditions. A clear evidence of over-curing state is the decrease in both tensile strength and elongation at break. A similar situation can be observed for plastisols cured at 205 °C.

Regarding to the Young's modulus (Fig. 1c), no significant changes are observed by curing with low temperatures profiles ( $T < 190$  °C). Nevertheless, for curing temperatures over 205 °C, we observed a clear increasing tendency in the Young's modulus as the curing time increases. Thus, plastisols cured at 220 °C for 17.5 min offer a Young's modulus close to 450 MPa which is in the typical range of these type of materials.

By taking into account tensile strength and elongation at break values, it can be concluded that under our test conditions, curing the plastisols at a temperature of 220 °C for 10 min provides cured plastisols with optimum-balanced properties. These results are in total agreement with previous studies as reported by Fenollar *et al.*<sup>29</sup> An interesting combination of maximum elongation at break (near 160 %) and high tensile strength values (over 11 MPa) has been obtained. Nevertheless, it is critical not to exceed the curing time, as a remarkable decrease in mechanical performance will occur.

### **Figure 1**

Table 1 shows a comparison of the main parameters (amount of plasticizer, curing conditions, sheet size and mechanical properties) of ECSO and different

epoxidized vegetable oils and several commercially available phthalates in plasticized PVC formulations. Results of tensile strength and elongation at break show similar values of ECSO providing an overview of the potential use of this biobased plasticizer.

### **Table 1.**

#### ***3.2.- Influence of the curing conditions on plastisol structure.***

Analysis of surface morphology of fractured samples from tensile tests is a useful technique to check the optimum curing conditions. As described previously, the plastisol gelation is a process in which a liquid PVC-plasticizer dispersion is converted into a flexible solid. To achieve optimum mechanical performance, gelation has to complete several stages that require combination of high temperatures and times<sup>26</sup>. Fig. 2 and Fig. 3 show SEM images of the surfaces of fractured samples from tensile tests for the lowest (7.5 min) and the highest (17.5 min) curing times respectively. For short curing times and relatively low temperature profiles ( $T < 200^{\circ}\text{C}$ ) (Fig. 2a, 2b and 2c), we observe the presence of spherical shapes which can be attributable to swollen PVC particles with the epoxidized cottonseed oil (ECSO) plasticizer but a homogeneous-continuous polymer matrix cannot be identified. This is representative of incomplete curing (under-cured plastisol). Individual swollen PVC particles can be detected; nevertheless, as the curing time and/or temperature increases, no spherical shapes are observed thus indicating that the curing process has been complete and a homogeneous matrix can be obtained so that, the plasticizer has been fully absorbed. For a particular curing cycle of  $190^{\circ}\text{C}$  and 7.5 min (Fig. 2c) slight presence of spherical shapes on the fractured surface can be observed. The effect of curing time is evident if we compare this structure with the sample corresponding to a curing cycle of  $190^{\circ}\text{C}$  for 17.5 min

(Fig. 3c), which is characterized by a clear homogeneous surface without spherical shapes; this fact is indicative of optimum gelation-curing process and, consequently, good mechanical properties as described before<sup>31</sup>. For curing temperatures over 205 °C (Fig. 2g, 2e, 3d and 3e), the fractured surfaces do not show presence of free plasticizer and spherical shapes thus indicating that the gelation is complete<sup>32</sup>. The degradation effects because of exposure to high temperature-time profiles can be observed in Fig. 3e in which, dark regions can be observed due to plasticizer remove and/or thermal degradation of PVC subjected to high temperature.

## **Figure 2**

## **Figure 3**

Optimum curing conditions can also be assessed by the solvent extraction test. A fully cured material is characterized by low migration in comparison to under-cured plastisol. Fig. 4 shows different plots of the migration evolution in terms of the curing time and isothermal curing temperatures for different migration times. As one can see the maximum migration levels are observed for PVC plastisols subjected to mild curing conditions (160 °C-7.5 min or 175 °C-7.5 min). Fig. 4a shows the evolution of the migration levels at 30 °C in terms of the curing times for the curing temperatures comprised between 160 °C and 220 °C. The highest migration values at 2 h are close to 7.6% and correspond to a curing profile of 160 °C and a curing time of 7.5 min. For this particular curing conditions, migration increases as the migration time increases thus leading to a remarkable migration level of 17.64% at 8 h. With regard to cured plastisols subjected to a curing profile of 175 °C for 7.5 min, the migration levels are 3.03% and

11.53% for migration times of 2 and 8 h respectively. By comparing these migration values with the abovementioned migration values corresponding to curing cycles of 160°C-7.5 min, we see a clear decrease in the migrated plasticizer.

A negative migration (swelling) was observed for plastisols cured at temperatures over 190 °C or at slower curing temperatures for curing times above 12.5 °C. The percentage weight gain due to swelling is low, no more than 2.5% for plastisols cured at 160 °C for 17.5 min and did not undergo migration. It is difficult to ensure that there is not free plasticizer for these particular curing conditions as the overall effect is swelling but actually two competing phenomena occur simultaneously. On the one hand, plasticizer extraction by the solvent action and on the other hand, plastisol swelling due to the entrance of some solvent inside the plastisol structure. The overall effect of these two competing processes is a very slight weight gain. Finally, swelling shows similar tendency for plastisols subjected to more aggressive migration cycles as observed in Fig 4b, 4c and 4d.

#### **Figure 4**

Temperature is another important factor to be considered for plasticizer extraction results. As the temperature for the solvent extraction tests increases, we observe a clear increase in the total extracted plasticizer (Table 2). To see migration values in detail curing profiles of 160 °C and 175 °C for 7.5 min were selected as they give clear evidence of the effect of both temperature and curing time on overall migrated mass weight.

#### **Table 2.**

For example, for plastisols cured at 160 °C for 7.5 min, the solvent extraction test at different temperatures gives the following results. For a solvent extraction test at 30 °C, the initial extracted plasticizer amount is 7.60% and this value is remarkably increased up to values of 21.71% for a testing temperature of 60 °C thus indicating the effect of temperature on plasticizer extraction which could be an important issue from a technical point of view as not fully cured plastisols are more sensitive to extraction and potential migration and this effect is even more accentuated by temperature. As describe before, extraction of plastisols cured at 175 °C is lower than that observed for plastisols cured at 160 °C. Nevertheless, we observe the same tendency with a clear increase in extraction levels as the testing temperature increases. Obviously, as the extraction time increases, the total extracted plasticizer also increases as it can be seen in Table 2 for extraction times of 2, 4, 6 and 8 h.

As we have described previously, incomplete curing of a plastisol leads to presence of free plasticizer. This can be observed by thermal analysis of cured materials. Fig. 5 shows a comparative plot of different DSC thermograms for cured plastisols subjected to different curing cycles. The endothermic peak located between -5 and 5 °C is attributable to the melt peak of free plasticizer as observed by other authors<sup>29</sup>. As the curing conditions reach the optimum, a decrease in the peak area is detected thus indicating less free plasticizer. For the mildest curing conditions used in this study (160 °C - 7.5 min) we see a peak at 2.4 °C which is representative for free epoxidized cottonseed oil (ECSO) plasticizer which has not participated in the swelling process of individual PVC particles, so that it remains as free plasticizer. Nevertheless, for more aggressive conditions, we do not see the peak located at 2 °C so that, it is indicating that the plasticizer has been fully absorbed by the individual PVC particles to form a gel structure. With regard to the glass transition temperature, the T<sub>g</sub> for

unplasticized PVC, which is typically of 87 °C<sup>22</sup> is decreased up to values below room temperature thus giving highly flexible materials. For longer curing times (17.5 min), an enhance in the T<sub>g</sub> was observed which was related to an improvement of the mechanical properties. As described previously, short curing times and low temperatures (7.5 min-160 °C) offered the worst mechanical properties and the highest migration values. The partially cured plastisol has similar behavior to that of a wax with poor consistency. It can be concluded that T<sub>g</sub> lower than -22 °C indicates poor mechanical properties and higher migration values due to high amounts of free plasticizer that does not interact with PVC polymer chains; on the other hand, a T<sub>g</sub> above -15 indicates absence of free plasticizer and is representative for fully cured PVC plastisols.

### **Figure 5**

#### ***3.3.- Influence of the curing time and temperature on final color of cured PVC plastisols.***

PVC is highly sensitive to thermal degradation. One of the most evident signs of this degradation is yellowing and browning. Obviously, the curing conditions govern the physical and chemical changes during the curing process but they also can affect the final appearance of the cured plastisol due to changes in color because of the exposure to more aggressive thermal conditions (high temperature during short time periods or moderate temperatures with long exposure times). Fig. 6 shows a matrix representation of the color appearance of the cured plastisols subjected to different curing cycles in terms of isothermal curing temperature and time. As we can see, mild curing conditions (160 °C and 175 °C and short curing times of 7.5 and 10 min) lead to an intense white color (fully opaque) but these conditions provide cured plastisols without good

mechanical properties as described previously. In fact, some of these cured plastisols could not be tested because they broke immediately, even with small pre-load application. As temperature and time increases, cured plastisols become translucent with a slight yellow color due to the intrinsic color of the plasticizer. This appearance indicates that the curing process has been completed. For aggressive curing conditions (205 °C - 15 min or 220 °C - 12.5 min) we observe a clear brownish color on cured plastisols which is indicative of thermal degradation. In addition to this change in color, a reduction of mechanical performance is detected because of plasticizer removal and PVC degradation. The cured plastisol subjected to the most aggressive conditions of this work (220 °C - 17.5 min) is completely dark brown and opaque. So that, the color of the cured plastisol together with its translucency can be useful from quality control since a simple observation of the final color could indicate the potential degradation during the curing cycle.

### **Figure 6**

By comparing the luminance values of the cured PVC plastisols, which describes the amount of light that is able to pass across the plastisol, it is possible to evaluate the curing state: under-cured, fully cured and not degraded and cured and degraded (over- cured). As the curing time increases, the luminance ( $L^*$ ) values decrease thus leading to more transparent materials. For cured PVC plastisols subjected to a curing temperature of 160 °C the luminance changes from 80% to 45% for curing times of 7.5 min and 17.5 min respectively. PVC plastisols cured at 175 °C offer a change in luminance from 72% (7.5 min) up to 42% (17.5 min) and this range is still narrower for PVC plastisols cured at 190 °C which suffers a decrease in luminance from

55% (7.5 min) to 40% (17.5 min). By taking into account the mechanical performance described previously, we can correlate the luminance values with the curing degree. So that, luminance values around 40 are representative for fully cured plastisols and not degraded. Luminance values over 50 units indicate partially cured plastisols (under cured material) while luminance values under 30 are representative for thermal degradation of cured plastisol.

### **Figure 7**

Additionally, the color coordinates  $a^*$  and  $b^*$  can be useful for quality control as it is possible to determine the curing degree of the PVC plastisol by relating these color coordinates with the previous mechanical results. These color coordinates change from red (positive  $a^*$  values) to green (negative  $a^*$  values) and from yellow (positive  $b^*$  values) to blue (negative  $b^*$  values). Fig. 8 shows a plot representation of the  $a^*b^*$  color space; this graph can be useful for quality control of cured plastisols as it is possible to identify different curing degrees as established before. By taking into account the mechanical performance of cured plastisols, SEM analysis and solvent extraction tests, the area corresponding to partially cured (under-cured) plastisols is characterized by  $a^*$  values comprised in the -4 to 0 and  $b^*$  values in the 2-11 range. Fully cured plastisols (and not degraded) are characterized by  $a^*$  values between 1 and 9 and an increase in  $b^*$  up to 20 (this area considers all the curing conditions corresponding to cured plastisols with the best performance). Over-cured plastisols (thermally degraded) are characterized by  $a^*$  values in the 6-13 range and low  $b^*$  values comprised between 2 and 10. This technique is very useful as it has been described in previous works with commercial epoxidized vegetable oils such as linseed oil<sup>27,29</sup>.

## Figure 8

### 4.- Conclusions.

Epoxidized cottonseed oil (ECSO) can be used as plasticizer to give partially biobased PVC plastisols. The curing conditions play a critical role on final performance of cured plastisols. A curing profile of 220 °C and 10 min seems to be the optimum in terms of the best mechanical performance; nevertheless, as PVC is highly sensitive to thermal degradation, the use of lower temperature and higher curing times such as 205 °C for 15 min could be an interesting solution as the curing conditions are not as aggressive. It is possible to obtain cured PVC plastisols with high elongation at break values (over 150%) which can compete with other plasticized PVC materials. From a quality control point of view, a simple study of the color coordinates gives enough information about the curing degree of plastisols cured at different conditions. Solvent extraction tests are also useful to assess the optimum conditions since partially cured plastisols are characterized by presence of free plasticizer that can easily migrate. In general terms, it is possible to obtain high environmentally low migration PVC plastisols by using epoxidized cottonseed oil as plasticizer.

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## References

1. Ali, M.; Ueki, T.; Hirai, T.; Sato, T.; Sato, T., *Polymer International* **2013** 62, 501.
2. Wang, F.; Yao, W.-g.; Qiao, C.-d.; Jia, Y.-x., *Acta Polymerica Sinica* **2012**, 1035.
3. Marcilla, A.; Garcia, J. C.; Ruiz, R.; Sanchez, S.; Vargas, C.; Pita, L.; Beltran, M. I., *International Polymer Processing* **2005** 20, 47.
4. Prowse, C. V.; de Korte, D.; Hess, J. R.; van der Meer, P. F.; Biomed Excellence Safer, T., *Vox Sanguinis* **2014** 106, 1.
5. Coltro, L.; Pitta, J. B.; da Costa, P. A.; Favaro Perez, M. A.; de Araujo, V. A.; Rodrigues, R., *Food Control* **2014** 44, 118.
6. Bueno-Ferrer, C.; Garrigos, M. C.; Jimenez, A., *Polymer Degradation and Stability* **2010** 95, 2207.
7. Chiellini, F.; Ferri, M.; Morelli, A.; Dipaola, L.; Latini, G., *Progress in Polymer Science* **2013** 38, 1067.
8. Coltro, L.; Pitta, J. B.; Madaleno, E., *Polymer Testing* **2013** 32, 272.
9. Zoller, A.; Marcilla, A., *Journal of Applied Polymer Science* **2011** 121, 1495.
10. Bouchoul, B.; Benaniba, M. T.; Massardier, V., *Journal of Vinyl & Additive Technology* **2014** 20, 260.
11. Veiga-Santos, P.; Oliveira, L. M.; Cereda, M. P.; Alves, A. J.; Scamparini, A. R. P., *Food Hydrocolloids* **2005** 19, 341.
12. Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C., *Polymer Testing* **2008** 27, 221.
13. Fenollar, O.; Garcia-Sanoguera, D.; Sanchez-Nacher, L.; Lopez, J.; Balart, R., *Journal of Materials Science* **2010** 45, 4406.
14. Ghiou, N.; Benaniba, M. T., *International Journal of Polymeric Materials* **2010** 59, 463.

15. Mehta, B.; Kathalewar, M.; Sabnis, A., *Polymer International* **2014** 63, 1456.
16. "Oilseeds: World Markets and Trade". Report from the United States Department of Agriculture, Foreign Agricultural Service, March 2016.
17. Jimenez, A.; Lopez, J.; Iannoni, A.; Kenny, J. M., *Journal of Applied Polymer Science* **2001** 81, 1881.
18. Fugit, J. L.; Taverdet, J. L.; Gauvrit, J. Y.; Lanteri, P., *Polymer International* **2003** 52, 670.
19. Manfredi, L. B.; Jimenez, A.; Vazquez, A., *Polymer International* **2005** 54, 576.
20. Leng, G.; Koch, H. M.; Gries, W.; Schuetze, A.; Langsch, A.; Bruening, T.; Otter, R., *Toxicology Letters* **2014** 231, 282.
21. Lindstrom, A.; Hakkarainen, M., *Journal of Applied Polymer Science* **2006** 100, 2180.
22. Yu, B. Y.; Lee, A. R.; Kwak, S.-Y., *European Polymer Journal* **2012** 48, 885.
23. Koch, H. M.; Muller, J.; Angerer, J., *Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences* **2007** 847, 114.
24. Daniels, P. H., *Journal of Vinyl & Additive Technology* **2009** 15, 219.
25. Verdu, J.; Zoller, A.; Marcilla, A., *Journal of Applied Polymer Science* **2013** 129, 2840.
26. Lopez, J.; Balart, R.; Jimenez, A., *Journal of Applied Polymer Science* **2004** 91, 538.
27. Fenollar, O.; Garcia, D.; Sanchez, L.; Lopez, J.; Balart, R., *European Polymer Journal* **2009** 45, 2674.
28. Carbonell-Verdu, A.; Bernardi, L.; Garcia-Garcia, D.; Sanchez-Nacher, L.; Balart, R., *European Polymer Journal* **2015** 63, 1.

29. Fenollar, O.; Sanchez-Nacher, L.; Garcia-Sanoguera, D.; Lopez, J.; Balart, R., *Journal of Materials Science* **2009** 44, 3702.
30. Karmalm, P.; Hiertberg, T.; Jansson, A.; Dahl, R.; Ankner, K., *Polymer Degradation and Stability* **2009** 94, 1986.
31. Zoller, A.; Marcilla, A., *Journal of Applied Polymer Science* **2011** 121, 3314.
32. Kwak, S. Y., *Journal of Applied Polymer Science* **1995** 55, 1683.

### **Table captions**

**Table 1.-** Comparison of the mechanical properties of cured PVC plastisols with different plasticizers: epoxidized cottonseed oil (ECSO), epoxidized linseed oil (ELO), epoxidized soybean oil (ESBO), diisononyl phthalate (DINP), bis(2-ethylhexyl) phthalate (DEHP) and dioctyl phthalate (DOP).

**Table 2.-** Percentage plasticizer migration for PVC cured plastisols subjected to different curing cycles in terms of the solvent extraction test with *n*-hexane in terms of migration time and temperature.

## **Figure legends**

**Figure 1.-** Mechanical properties of PVC plastisols plasticized with epoxidized cottonseed oil (ECSO) in terms of the curing time for different isothermal curing temperatures a) tensile strength, b) elongation at break, c) Young's modulus.

**Figure 2.-** SEM images (250x) of surfaces of fractured samples from tensile tests of cured PVC plastisols subjected to curing cycles of 7.5 min and temperatures of a) 160 °C, b) 175 °C, c) 190 °C, d) 205 °C and e) 220 °C.

**Figure 3.-** SEM images (250x) of surfaces of fractured samples from tensile tests of cured PVC plastisols subjected to curing cycles of 17.5 min and temperatures of a) 160 °C, b) 175 °C, c) 190 °C, d) 205 °C and e) 220 °C.

**Figure 4.-** Migration levels (weight percentage gain) of cured PVC plastisols with ECSO plasticizer subjected to different curing cycles at different migration temperatures a) 30 °C, b) 40 °C, c) 50 °C and d) 60 °C.

**Figure 5.-** Comparative DSC curves of cured PVC plastisols plasticized with ECSO subjected to different curing cycles.

**Figure 6.-** Optical photographs of cured PVC plastisols with ECSO plasticizer subjected to different curing conditions in terms of the isothermal curing temperature and curing time.

**Figure 7.-** Contour plot of the luminance of cured PVC plastisols with ECSO plasticizer in terms of the isothermal curing temperature and curing time.

**Figure 8.-** Variation of the color coordinates  $a^*b^*$  of cured PVC plastisols with ECSO plasticizer subjected to different curing conditions.