

## Optimization of the curing conditions of PVC plastisols plasticized with ethyl cinnamate

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### ABSTRACT

The use of ethyl cinnamate, an ester of cinnamic acid present in many fruits and plants, as a bio-based plasticizer for polyvinyl chloride (PVC) plastisols has been investigated. Different temperatures (180, 190, and 200 °C) and curing times (8, 11.5, and 15 min) have been evaluated for PVC plasticized with 70 phr (parts by weight of plasticizer per one hundred weight parts of PVC resin) of ethyl cinnamate in order to optimize the curing conditions of the material, as these play a fundamental role in determining the final properties. Optimization of curing conditions has been carried out by analyzing the effect of temperature and curing time on the tensile mechanical properties, thermal stability, morphological, color changes, and migration tendency for the different plasticized materials. It has been observed that the optimal curing conditions for PVC plasticized with ethyl cinnamate are achieved at a curing temperature of 190 °C and a curing time of 11.5 min. Under these conditions, a material with high tensile strength, around 6.4 MPa, and a high elongation at break, close to 570 %, is obtained which is comparable or even superior to materials cured in the presence of other conventional plasticizers used in the PVC industry. Additionally, through field emission scanning electron microscopy (FESEM), it has been observed that for these conditions, the curing process is complete, resulting in the complete fusion of PVC microcrystals. A material with high cohesion and very low migration loss, around 2.4 %, is obtained. The effectiveness of these curing conditions has also been demonstrated using thermogravimetry. An increase in the PVC dehydrochlorination temperature has been observed due to optimum plasticizer absorption and gelation.

### 1. Introduction

Polyvinyl chloride (PVC) is one of the most widely produced and consumed polymers globally due to its mechanical properties when it is plasticized, versatility, and low cost [1,2]. Because of these characteristics, PVC has been widely used in a variety of sectors such as construction, automotive, food packaging, toys production, the electrical industry, medicine, and agriculture [3]. PVC is a hard and rigid polymer due to the presence of a dipole in each C-Cl bond and the interaction between PVC chains, which hinders mobility [4]. This is the reason why additives such as plasticizers are incorporated into PVC to improve its flexibility and processability. These plasticizers form secondary interactions with the polymeric chains through dipole-dipole interactions

and increase the intermolecular free volume, preventing PVC molecules from approaching each other, thereby increasing the flexibility [5,6]. Currently, it is estimated that one-third of the PVC consumed worldwide is in the form of flexible PVC, used in everyday items such as cable coatings, toys, food packaging, footwear components, blood bags, etc. [7].

There is a wide variety of plasticizers available for the production of flexible PVC, including citrates, adipates, azelates, benzoates, and phosphates [8]. However, plasticizers from the phthalate family are among the most widely used in PVC plasticization due to their performance and low cost, representing 75 % of the plasticizer market [9]. Among them, the use of di-2-ethylhexyl phthalate (DEHP), also known as dioctyl phthalate (DOP), is most prominent. However, one of the main

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limitations of such plasticizers is that they tend to migrate to the surface over time due to the lack of chemical bonding between the plasticizer and PVC and their low molecular weight [10,11], they may escape the polymer matrix and come into contact with consumers and the environment. Health and environmental degradation due to toxicity may result [12]. Additionally, current European regulations prohibit the use of certain types of phthalate plasticizers in specific applications such as the production of toys, food packaging, medical devices, and childcare products [13]. This has led to increased interest in finding safe alternatives to these plasticizers. Numerous examples of the use of biobased and non-toxic plasticizers for producing flexible PVC have been reported. Among these plasticizers are epoxidized vegetable oils, such as epoxidized soybean oil [14–16], epoxidized linseed oil [17,18], epoxidized sunflower oil [19,20] or epoxidized cottonseed oil [21]. Also, some ethers have been investigated, such as epoxidized cardanol glycidyl ether or hydrogenated cardanol glycidyl ether [22]. These plasticizers have shown good effectiveness for PVC plasticization, their presence improving flexibility and toughness. They may be particularly useful as secondary plasticizers [23]. Additionally, it has been observed that some of these plasticizers increase the thermal stability of the material because the epoxy groups they contain are capable of consuming the HCl generated during PVC degradation. Therefore, the presence of epoxidized oils may moderate PVC dehydrochlorination to maintain color and reduce PVC property loss at high temperatures [16,24]. In addition, newer strategies have been researched for preventing plasticizer migration in PVC, such as hyperbranching, for example using hyperbranched polyglycerol on PVC. This structure difficults the exit of the plasticizer from the PVC structure. Another promising group of biobased plasticizers for PVC are esters derived from natural acids, such as cinnamic acid esters. The plasticizing effect of different cinnamic acid esters in PVC has been reported [25]. Incorporation of 50 phr of these cinnamates results in efficient plasticization. Materials with elongations at break exceeding 260 % and tensile strengths between 9.6 and 22.2 MPa may be obtained. Highly branched materials, in particular, hyperbranched oligomeric esters of glycerol and adipic acid are highly effective plasticizers for PVC.

Plasticization plays a fundamental role in the complex curing process of plastisols. A plastisol is a suspension of PVC resin particles in a liquid phase composed mainly of plasticizer, although other additives such as colorants, thermal stabilizers, or fillers may be incorporated [26]. These plastisols are generally viscous at room temperature and become a solid material with elastomeric properties when heated to appropriate temperatures [27]. This process is known as curing and consists of different stages. Firstly, the gelation stage takes place, heating the suspension causes the plasticizer to diffuse between the gaps and promotes aggregation of PVC particles, solvating the non-crystalline parts of the polymer chain and causing the resin particles to swell, reducing the amount of free plasticizer [28]. The most significant changes in this initial stage occur around 80–100 °C, coinciding with the glass transition temperature of PVC, as increased mobility of the polymer chains favors plasticizer diffusion and its interaction with the resin [27]. In this stage, the material absorbs all the plasticizer, acquiring a gel structure with low structural cohesion and no industrial utility. Secondly, the fusion stage occurs, which takes place between 160 and 190 °C [27]. In this stage, the plasticizer produces solvation (fusion) of the crystalline parts of PVC, allowing the polymer chains to acquire greater mobility and interact with polymer chains from other resin particles [21]. Finally, the last stage of the curing process, cooling, takes place. In this stage, the microcrystals are formed again, crosslinking the polymer chains [29]. The intertwining of the polymer chains along with the interactions between them result in a material with good mechanical strength. On the other hand, the plasticizer dissolves the amorphous parts of the polymer, giving it excellent flexibility [5]. Therefore, once cooled, the material obtained has high cohesion and high ductility, although the final properties of the material will largely depend on the curing temperature and time.

Optimization of the curing conditions of PVC plasticized with ethyl cinnamate, an ester of cinnamic acid and ethanol found in many plants or fruits, such as cinnamon or strawberries, as a biobased plasticizer for PVC plastisols has been evaluated. This plasticizer was chosen due to it being an environmentally friendly plasticizer, and due to offering more promising results than other cinnamates in preliminary studies. More specifically, PVC plastisols with a constant plasticizer content of 70 phr were obtained and subjected to different curing temperatures (180 °C, 190 °C, and 200 °C) and times (8, 11.5, and 15 min). The effect of curing conditions on the properties of PVC plastisols plasticized with ethyl cinnamate was determined through characterization of mechanical, thermal, morphological, optical, and migration properties. The results of this study can pave the way for future studies in which new additives can be added to this plasticized PVC.

## 2. Experimental

### 2.1. Materials

Polyvinyl chloride (PVC) resin grade Lacovyl PB 1172 H was provided by Atofina UK, Ltd, (Midlands, UK) with a kwert (k) value of 67 determined according to ISO 1628-2. Ethyl cinnamate (purity >95 %) was used as PVC plasticizer, which was supplied by Merck S.L.U. (Madrid, Spain). This plasticizer is characterized by a density of 1.049 g ml<sup>-1</sup>, a molecular weight of 176.2 g mol<sup>-1</sup>, a melting point between 6 and 8 °C and a boiling point of 271 °C. The chemical structure of ethyl cinnamate is shown in Fig. 1.

### 2.2. Sample processing

The different PVC plastisol formulations were prepared following the process described by Fenollar et al. [30]. For this purpose, PVC powder and ethyl cinnamate were placed in a container with a weight ratio of 100:70. Subsequently, both components were mixed using a BOMANN rotary mixer mod. KM 315 CB (BOMANN, Madrid, Spain) in order to

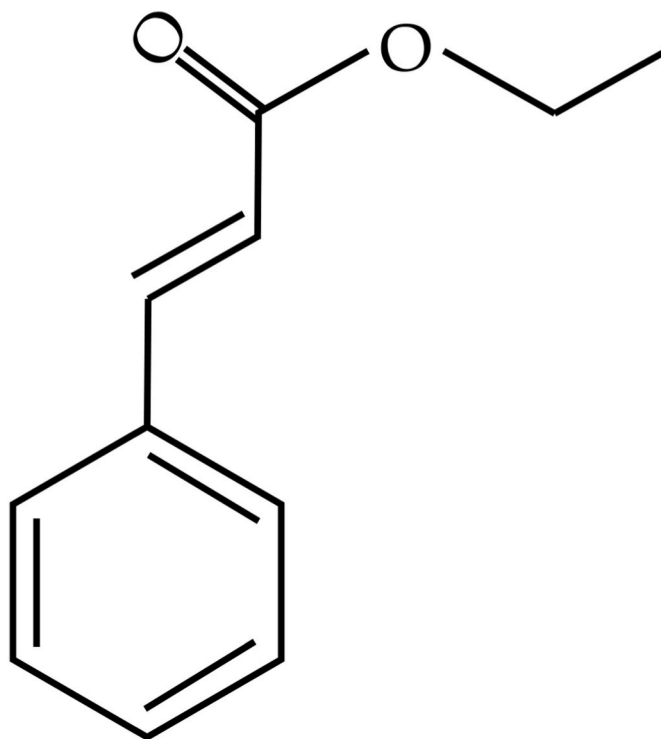


Fig. 1. Chemical structure of the ethyl cinnamate used as bio-based plasticizer for polyvinyl chloride (PVC).

obtain a homogeneous paste. After mixing both components, the plastisol mixture was degassed in a vacuum chamber VACIOTEM-T from JP Selecta (Barcelona, Spain) for 2 h to remove bubbles from the inside of the paste. After degassing, the mixture was poured into rectangular aluminium molds with a size of  $300 \times 190 \text{ mm}^2$  and a wall thickness of 0.8 cm. Liquid plastisol was introduced in the amount required to achieve a thickness of 4 mm. Finally, the curing process was carried out in an air circulating oven model Selecta 2001245 (JP Selecta S.A., Barcelona, Spain) at different temperatures (180 °C, 190 °C and 200 °C) and with different curing times (8, 11.5 and 15 min) for each temperature. From the cured samples, standardized specimens were obtained using a die and a hydraulic press mod. MEGA KCK-15A (Melchor Gabilondo S. A., Vizcaya, Spain). Table 1 shows the coding of the samples obtained with the temperatures and curing times used for each of them.

## 2.3. Characterization techniques

### 2.3.1. Mechanical characterization

The tensile mechanical properties of PVC plastisols plasticized with EC at different temperatures and curing times were obtained using a universal testing machine model Ibertest ELIB 30 from S.A.E. Ibertest (Madrid, Spain) equipped with a 5 kN load cell and a crosshead speed of  $20 \text{ mm min}^{-1}$ . The tests were performed according to ISO 527-2:2012 at room temperature with an initial length of 50 mm. A total of five specimens were tested for each obtained formulation, and the mean values of tensile strength and elongation at break were calculated.

Shore A hardness measurements for the cured PVC plastisols were carried out using a durometer model 673-D from J. Bot S.A. (Barcelona, Spain), following the ISO 868:2003 standard. For each of the formulations, at least 10 measurements were taken at different points of the sample, using the average value of these measurements as a reference for the hardness of each formulation.

### 2.3.2. Thermal characterization

The glass transition temperature ( $T_g$ ) of PVC plastisols was obtained by differential scanning calorimetry (DSC), using a DSC model DSC25 from TA Instruments (New Castle, USA). The samples, weighing between 5 and 7 mg, were first subjected to a cooling cycle from 25 °C to -80 °C at a rate of  $-5 \text{ °C min}^{-1}$  and then a heating cycle from -80 °C to 60 °C at a constant rate of  $5 \text{ °C min}^{-1}$  in nitrogen atmosphere (flow rate  $66 \text{ mL min}^{-1}$ ).

Thermal stability at high temperatures of the cured PVC plastisols was evaluated using thermogravimetric analysis in a TG-DSC2 thermobalance from Mettler-Toledo (Columbus, OH, USA). Samples weighing between 5 and 7 mg were subjected to a heating cycle from 30 °C to 600 °C with a rate of  $10 \text{ °C min}^{-1}$  under nitrogen atmosphere (flow rate  $66 \text{ mL min}^{-1}$ ). The main degradation temperature ( $T_{max}$ ) of each cured PVC plastisol was obtained from the peak maximum observed in the first derivative of TGA curves (DTG).

**Table 1**

Designation of PVC plastisol formulations plasticized with ethyl cinnamate under different curing conditions.

Sample	Curing Temperature (°C)	Curing Time (min)
PVC-EC/180_8	180	8
PVC-EC/180_11.5	180	11.5
PVC-EC/180_15	180	15
PVC-EC/190_8	190	8
PVC-EC/190_11.5	190	11.5
PVC-EC/190_15	190	15
PVC-EC/200_8	200	8
PVC-EC/200_11.5	200	11.5
PVC-EC/200_15	200	15

### 2.3.3. Morphological characterization

Fracture morphology of the cured PVC plastisols subjected to tensile tests was evaluated using field emission scanning electron microscopy (FESEM). For this analysis a ZEISS ULTRA 55 FESEM microscope from Oxford instruments (Abingdon, United Kingdom) operated at a voltage of 2 kV was used. Prior to the morphological analysis, the samples were coated with a thin layer of gold-palladium alloy, using an EMITECH sputter coating SC7620 model from Quorum Technologies, Ltd.

### 2.3.4. Color properties

The effect of curing conditions on the surface color of the cured PVC plastisols was evaluated using the CIELAB color scale. Measurements were conducted with a Konica CM-3600d Colorflex-DIFF2 colorimeter from Hunter Associates Laboratory, Inc. (Virginia, USA) calibrated using a standard white tile. For each sample, the color coordinates  $L^*$  (lightness),  $a^*$  (red-green) and  $b^*$  (yellow-blue) were recorded at five random positions and mean values were calculated.

### 2.3.5. Migration test

The migration test in n-hexane solvent was carried out following the guidelines of ASTM D5227-21. For this purpose, samples weighing approximately 2.5 g of all the PVC plastisol formulations were immersed in n-hexane at a temperature of 49.5 °C for 2 h. Subsequently, the samples were placed in a vacuum oven at 80 °C for 2 h. Finally, the samples were weighed to measure the weight loss. This method assumes that the weight of the residual extract in n-hexane corresponds to the plasticizer extracted from the sample.

## 2.4. Statistical analysis

The significant differences among samples were evaluated at 95 % confidence level ( $p \leq 0.05$ ) by one-way analysis of variance (ANOVA) following Tukey's test. Additionally, a 3-level factorial ANOVA experiment design was carried out for optimizing the developed materials according to temperature and curing time taking into consideration the tensile strength and elongation at break.

## 3. Results and discussion

### 3.1. Mechanical properties of PVC plastisols subjected to different curing conditions

Mechanical properties of plastisols are highly influenced by their curing conditions. Fig. 2 shows the tensile strength and elongation at break of the different PVC plastisols obtained at different curing temperatures and times. It is worth noting that all the obtained materials exhibit high cohesion, indicating that the curing process has been completed in all of them. Regarding tensile mechanical properties, in the case of tensile strength (Fig. 2a), it can be observed that the highest strength is obtained for the sample cured at 190 °C for 11.5 min, where a value of 6.4 MPa is achieved. It can be deduced that under these conditions, a completely cured material is obtained, in which complete fusion of PVC microcrystals occurs and there is greater interaction between the particles, resulting in a material with high cohesion. For this temperature, 190 °C, it is observed that with curing times of 15 min, the strength slightly decreases to 5.8 MPa. However, this decrease is more notable with low curing times, 8 min, where a strength of 4.8 MPa is obtained, representing a decrease of 29.4 % compared to the sample cured at 11.5 min. For curing temperatures of 180 °C, Fig. 2a shows that tensile strength rises as curing time increases, reaching the highest tensile strength in the sample cured for 15 min (5.7 MPa). Finally, for curing temperatures of 200 °C, the highest tensile strength is obtained in the sample cured for 11.5 min, with a tensile strength of 5.4 MPa. Longer curing times (15 min) result in a significant decrease in tensile strength, reaching a value of 3.2 MPa. This is due to material degradation when subjected to high temperatures and long curing times.

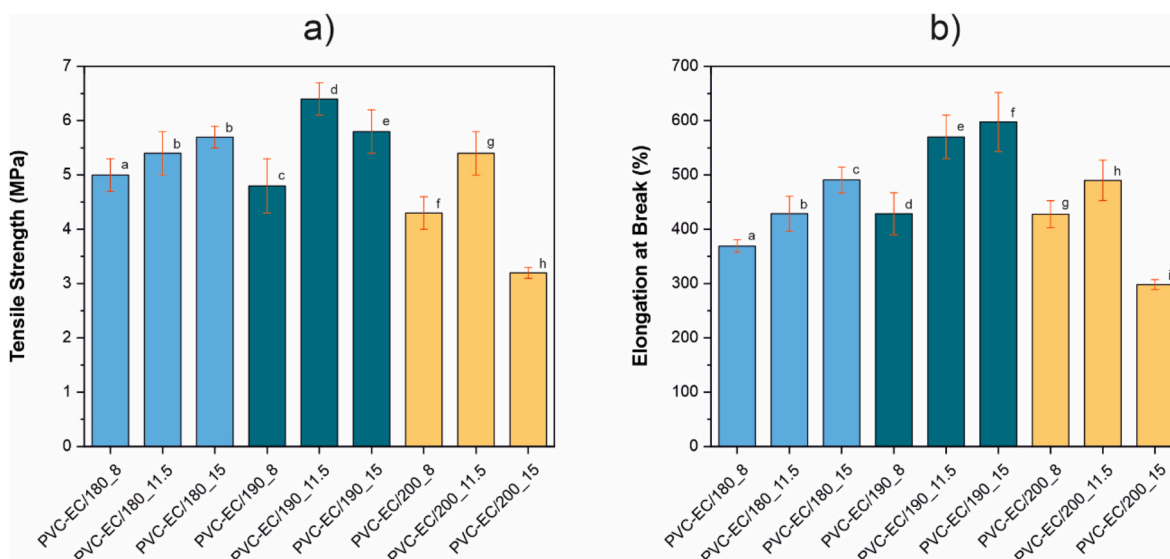


Fig. 2. Tensile mechanical properties of the PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times: a) tensile strength and b) elongation at break.

<sup>a-i</sup> indicates significant differences between the values obtained ( $p \leq 0.05$ ).

Regarding elongation at break, it can be observed in Fig. 2b that the obtained plastisols exhibit a similar trend to tensile strength. Elongation at break increases with curing time for the three studied curing temperatures except for the sample cured at 200 °C for 15 min, where a decrease in elongation at break compared to the sample cured at 11.5 min is observed. This decrease is due to over-curing of the sample, resulting in a reduction in both tensile strength and elongation at break.

In this case, the highest elongation at break is obtained for the sample cured at 190 °C for 15 min, with an elongation at break of 597.7 %, which represents an increase of approximately 40 % compared to the sample cured at 190 °C for 8 min. On the other hand, for curing temperatures of 180 °C, the highest elongation at break is 490.8 % for the sample cured for 15 min. For elevated curing temperatures, 200 °C, it is observed that elongation increases up to curing times of 11.5 min, with

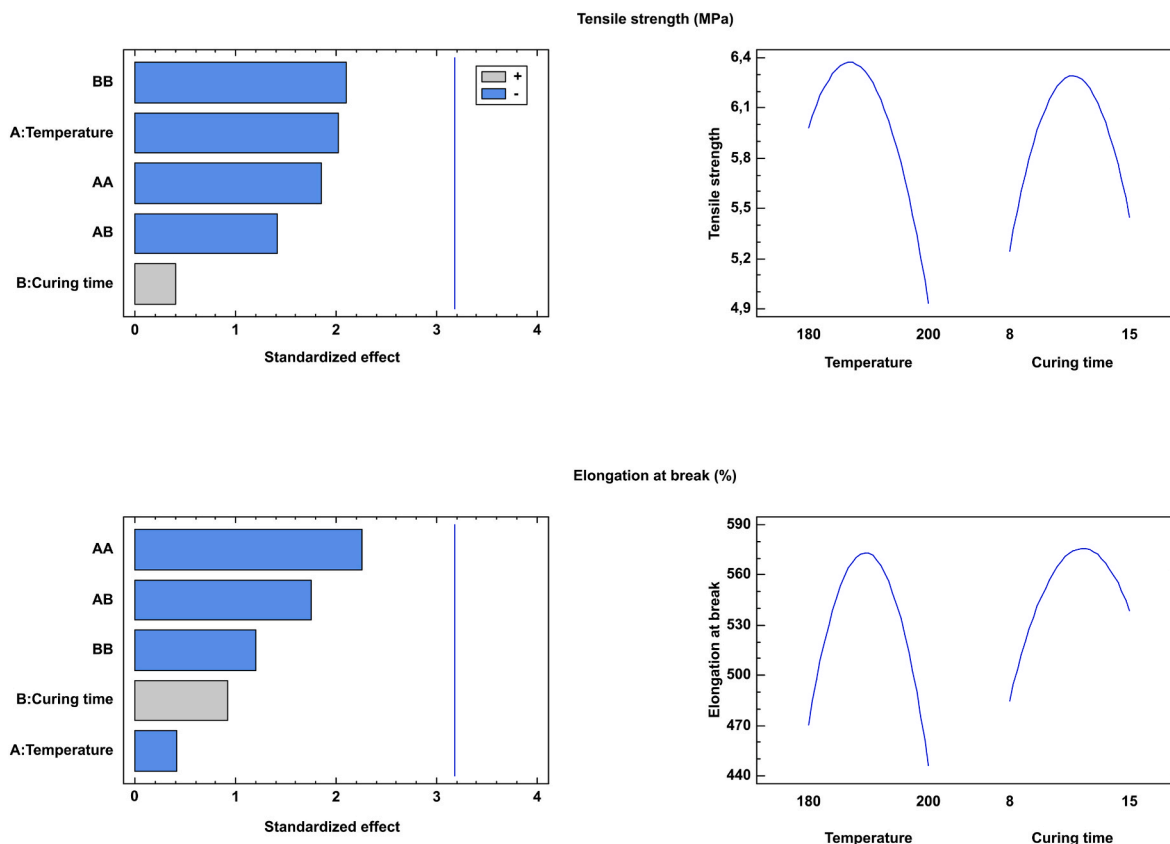


Fig. 3. Summary of the ANOVA analysis for the PVC plastisols plasticized with ethyl cinnamate. At the left, the Pareto diagram standardized effect is shown, while at the right, the main effects diagram is displayed. This was shown for tensile strength and elongation at break.

an elongation of 490.1 %, followed by a drastic decrease in elongation at break for longer curing times (15 min), reaching an elongation of 298.2 %. This decrease at high temperatures and long curing times indicates thermal degradation of the material. PVC-DOP plastisols have been reported to provide elongation at break values between 100 and 213 %, which is far below the ductile behavior herein reported [31]. Therefore, these results demonstrate the great potential of ethyl cinnamate as an excellent environmentally friendly plasticizer for PVC.

After analyzing the mechanical properties of the different PVC plastisols, it is deduced that for short curing times (8 min) at the three tested temperatures, the curing process is not fully completed, and therefore, the plastisol does not achieve adequate cohesion between the swollen particles, resulting in materials with lower mechanical strength and ductility [30]. On the other hand, prolonged curing times at high temperatures, 190 and 200 °C, cause some degradation of the material, leading to a decrease in its mechanical properties. In this case, a material with balanced properties is obtained when a curing temperature of 190 °C and a curing time between 11.5 and 15 min are employed. This is corroborated by the results obtained by the ANOVA analysis (Fig. 3), which clearly shows that the optimal temperature is 190 °C both for tensile strength and elongation at break, as well as an optimal curing time of 11.5 min for both parameters. At these parameters, there is a high absorption of the plasticizer and complete fusion of the PVC microcrystals, resulting in greater structural cohesion of the material and a greater plasticizing efficiency. Additionally, it is worth noting that the use of ethyl cinnamate as a plasticizer results in materials with high ductile properties, comparable to those obtained with the use of commercially available plasticizers, such as phthalates, which are not environmentally friendly [32–34]. On the other hand, it has been observed that ethyl cinnamate exhibits a greater plasticizing effect than other biobased plasticizers for equal plasticizer contents. Table 2 shows the optimal curing conditions, and the obtained mechanical properties (tensile strength and elongation at break) for different PVC plastisols plasticized with 70 phr of biobased plasticizers.

In Fig. 4, Shore A hardness of PVC plastisols subjected to different curing temperatures and times is shown. For curing temperatures of 180 and 190 °C, a similar trend is observed, as well as similar hardness values for each of the curing times. At curing times of 8 and 11.5 min, the samples have a hardness around 44 Shore A for both temperatures, increasing to 50 for curing times of 15 min. Among samples cured at 200 °C, it can be observed that the highest hardness is obtained in the sample cured at 8 min, with a value of 54 Shore A, while for longer curing times, 11.5 and 15 min, the hardness decreases to 50.

### 3.2. Thermal properties of PVC plastisols with different curing conditions

The effect of curing conditions on the thermal properties of PVC plastisols plasticized with ethyl cinnamate has been studied by DSC and TGA. In Fig. 5a, the calorimetric curves of PVC powder and ethyl cinnamate plasticizer are observed, while in Fig. 5b, the calorimetric curves of PVC plastisols obtained at different temperatures and curing times are shown. On the other hand, Table 3 shows the glass transition temperature ( $T_g$ ) of each of the PVC plastisols studied, which have been obtained from the calorimetric curves. The  $T_g$  is related to the polymer chain size,

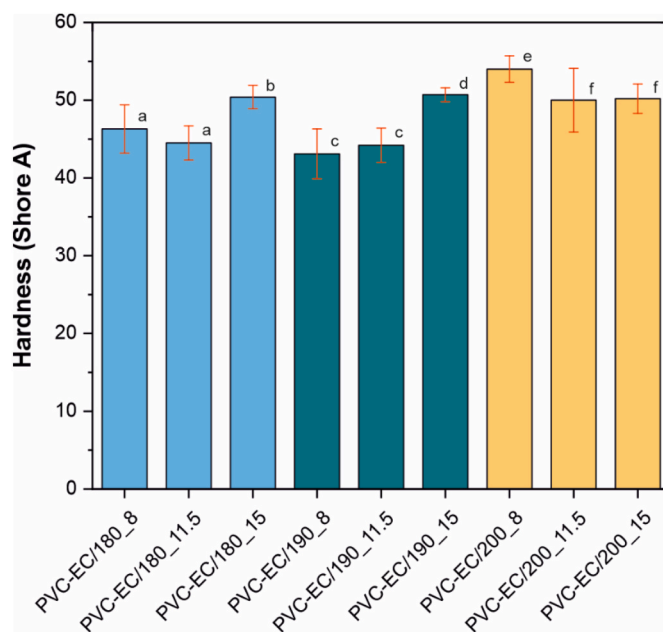


Fig. 4. Shore A hardness of the PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.

<sup>a-f</sup> indicates significant differences between the values obtained ( $p \leq 0.05$ ).

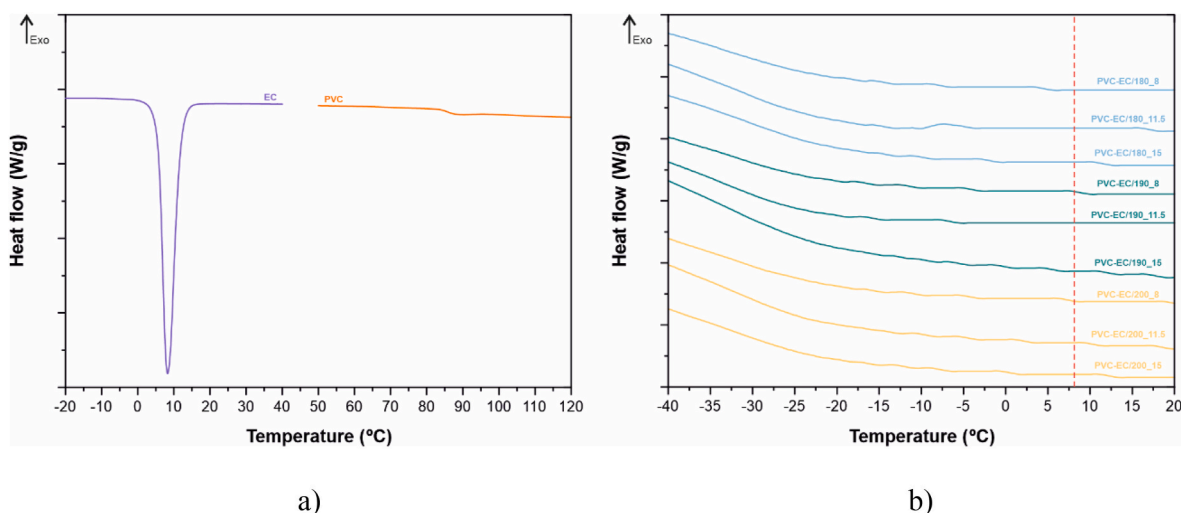
the attraction force between them, and the free volume between macromolecules [36]. Therefore, this parameter is of great interest when optimizing the curing conditions of plasticized PVC. In Fig. 5a, it can be observed that ethyl cinnamate has a melting point around 8 °C, while in none of the calorimetric curves of the plastisols is this melting peak of the plasticizer appreciated, indicating that the plasticizer has been completely absorbed by the PVC to form a gel structure for all studied curing conditions, and therefore there is no free plasticizer in any of the samples [21]. Regarding  $T_g$ , in Fig. 5a, it can be seen that unplasticized PVC has a  $T_g$  around 85 °C, while for plasticized PVC samples, the  $T_g$  decreases to values below  $-30$  °C, indicating that the plasticizer reduces the intermolecular forces between PVC chains, resulting in materials with high flexibility at room temperature. In this case,  $T_g$  values are very similar for all samples, although slight differences can be observed between them. As shown in Table 3, for samples cured at 180 and 190 °C,  $T_g$  rises as the curing time increases. That is, for plastisols cured at 180 and 190 °C, the lowest  $T_g$  is obtained for a curing time of 8 min, yielding values of  $-34.6$  and  $-37.3$  °C, respectively, increasing for materials cured for 15 min to  $-30.2$  and  $-35.5$  °C, respectively. This increase in  $T_g$  with curing time is related to an increase in mechanical properties, as observed previously. In the case of samples cured at 200 °C, it is observed that  $T_g$  increases from  $-36.1$  °C for the sample cured at 8 min to  $-34.8$  °C for the sample cured at 11.5 min; however,  $T_g$  decreases again to  $-37.5$  °C for the sample cured for 15 min, likely due to thermal degradation.

The thermal decomposition of the different cured PVC plastisols has been studied by thermogravimetric analysis (TGA). Fig. 6 shows the TGA

Table 2

Comparison of the mechanical properties of PVC plastisols plasticized with 70 phr of different bio-based plasticizers.

Plasticizer	Plasticizer content (phr)	Optimal curing temperature (°C)	Optimal curing time (min)	Tensile strength (MPa)	Elongation at break (%)	Reference
Ethyl Cinnamate	70	190	11.5	6.4	570.2	–
Epoxidized cotton seed oil	70	220	10	~11	~150	[21]
epoxidized fatty acid ester	70	220	10	~10	~250	[30]
	70	220	12	11.4	~275	[35]
epoxidized linseed oil	70	200	12	12.1	224	[18]



**Fig. 5.** Differential scanning calorimetry (DSC) curves of the second heating cycle of a) unplasticized PVC and ethyl cinnamate, and b) PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.

**Table 3**

Main thermal parameters of PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times obtained by differential scanning calorimetry (DSC) and thermogravimetry (TGA).

Sample	DSC		TGA	
	$T_g$ (°C)	$T_{maxI}$ (°C)	$T_{maxII}$ (°C)	$T_{maxIII}$ (°C)
PVC-EC/180_8	$-35.6 \pm 2.2^a$	$242.3 \pm 0.5^a$	$282.3 \pm 3.2^a$	$469.9 \pm 1.1^a$
PVC-EC/ 180_11.5	$-32.6 \pm 1.7^b$	$244.6 \pm 1.3^a$	$284.3 \pm 1.9^a$	$468.2 \pm 0.9^a$
PVC-EC/180_15	$-31.2 \pm 2.5^b$	$241.3 \pm 1.0^a$	$302.6 \pm 1.6^b$	$468.3 \pm 1.3^a$
PVC-EC/190_8	$-36.3 \pm 2.5^c$	$245.6 \pm 0.5^a$	$285.3 \pm 2.1^c$	$469.4 \pm 0.7^a$
PVC-EC/ 190_11.5	$-34.6 \pm 1.3^d$	$242.3 \pm 0.7^a$	$303.5 \pm 2.8^d$	$470.8 \pm 0.9^a$
PVC-EC/190_15	$-34.5 \pm 1.4^d$	$241.8 \pm 0.7^a$	$301.3 \pm 1.7^d$	$469.8 \pm 0.2^a$
PVC-EC/200_8	$-36.1 \pm 2.1^e$	$244.7 \pm 0.3^a$	$296.0 \pm 2.5^d$	$467.3 \pm 1.3^a$
PVC-EC/ 200_11.5	$-34.8 \pm 1.5^f$	$241.2 \pm 1.1^a$	$299.1 \pm 1.5^d$	$469.2 \pm 0.8^a$
PVC-EC/200_15	$-37.5 \pm 2.4^g$	$244.7 \pm 1.8^a$	$288.8 \pm 2.2^d$	$470.6 \pm 1.1^a$

<sup>a-g</sup> indicates significant differences between the values obtained ( $p \leq 0.05$ ).

curves and the first derivative of the TGA curves (DTG) of the PVC plastisols cured at different temperatures and curing times. On the other hand, Table 3 shows the temperatures of the main decomposition stages of the PVC plastisols. The degradation of PVC occurs in two stages: a first stage between 260 and 350 °C where dehydrochlorination takes place, resulting in the formation of C=C double bonds, which forms a structure of conjugated polyene and benzene by cyclization of unsaturated chain ends. The second stage of PVC degradation occurs at temperatures above 450 °C, where the decomposition of the polymeric chain and the benzene formed after dehydrochlorination takes place, resulting in short-chain alkanes or alkenes [37,38]. A very similar thermodegradation profile was observed in a study [39] for PVC plasticized with dioctyl phthalate (DOP), a typical plasticizer for PVC, exhibiting a maximum degradation rate temperature between 250 and 310 °C. On the other hand, ethyl cinnamate has a high boiling point, 271 °C, however, monomeric plasticizers are highly volatile and can vaporize at temperatures lower than their boiling point [40]. Observing Fig. 6b, in all the obtained plastisols, there is a first stage of degradation around 240 °C

( $T_{maxI}$ ), which is related to the volatilization of part of the plasticizer. This degradation stage overlaps with the first stage of PVC degradation ( $T_{maxII}$ ), which takes place between 280 °C and 305 °C. Finally, in the DTG curves of the plastisols, the second stage of PVC degradation can be distinguished ( $T_{maxIII}$ ) around 470 °C. In this case, as observed in Table 3, the different curing conditions of the plastisols hardly affect the volatilization of the plasticizer ( $T_{maxI}$ ), and to the second stage of PVC degradation ( $T_{maxII}$ ), obtaining very similar temperatures for all samples in both stages. However, it can be observed that the PVC dehydrochlorination temperature ( $T_{maxII}$ ) is indeed affected by the different curing conditions. In this case, it can be seen that the samples exhibiting better mechanical properties for each of the studied curing temperatures, and therefore greater structural cohesion, are those with higher degradation temperatures. This is evident in the sample cured at 180 °C for 15 min, where a degradation temperature of 302.6 °C is obtained, in the sample cured at 190 °C for 11.5 min, with a degradation temperature of 303.5 °C, and in the sample cured at 200 °C for 11.5 min, with a degradation temperature of 299.1 °C. Therefore, it can be inferred that the curing conditions affect the thermal stability of the material. Samples showing a higher fusion of PVC microcrystals and thus greater cross-linking between polymer chains after cooling exhibit better thermal stability, resulting in an increase in PVC dehydrochlorination temperature [27,41].

### 3.3. Morphological properties of PVC plastisols with different curing conditions

Morphological analysis of the PVC plastisols cured at different temperatures and times is shown in Fig. 7. In this case, the fracture surface of the various plastisol samples was evaluated using FESEM. As observed, none of the micrographs of the different obtained plastisols show PVC particles or aggregates, indicating a fully cohesive surface in all of them. This indicates that the curing process has occurred properly in all samples, with complete absorption of the plasticizer by the PVC particles and subsequent fusion of the PVC microcrystals [42]. However, slight differences can be observed among the different samples. In the case of samples cured at a temperature of 180 °C, some surface roughness can be seen, being more pronounced in the sample cured at the lowest temperature of 8 min (Fig. 7a). For longer curing times, this roughness decreases. Surface roughness can also be observed in the samples cured at 190 °C and 200 °C for 8 min (Fig. 7d and g). This may be due to incomplete fusion of the PVC microcrystals due to the low temperature and/or short curing times, resulting in lower material cohesion, which

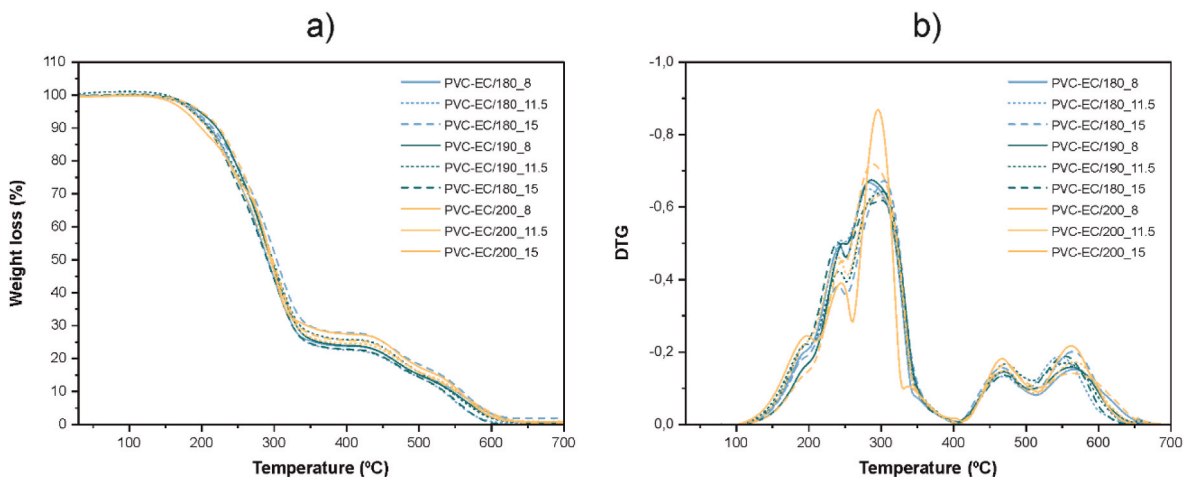


Fig. 6. Thermogravimetric curves (TGA) (a) and their first derivative (DTG) (b) of PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.

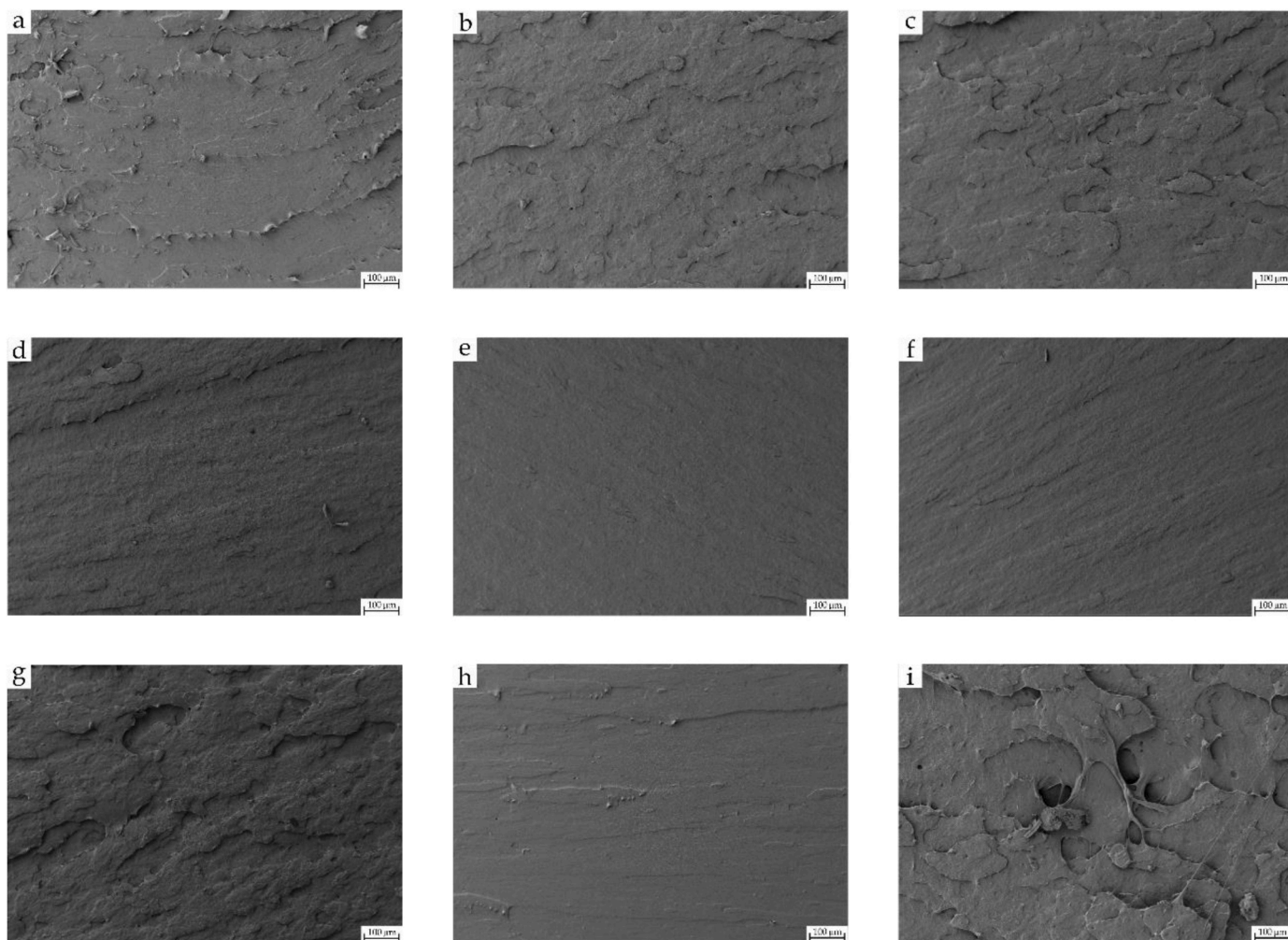


Fig. 7. FESEM micrographs at 100 × of PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.: a) PVC-EC/180\_8; b) PVC-EC/180\_11.5; c) PVC-EC/180\_15; d) PVC-EC/190\_8; f) PVC-EC/190\_11.5; g) PVC-EC/190\_15; h) PVC-EC/200\_8 and i) PVC-EC/200\_11.5.

affects the mechanical properties of the material, as evidenced by lower mechanical properties [43]. On the other hand, it can be observed that the samples cured at 190 °C for 11.5 and 15 min (Fig. 7e and f) present a completely smooth and homogeneous surface. This is indicative of an

optimal curing process, where complete fusion of the PVC microcrystals occurs, achieving high structural cohesion with strong interactions between the particles, resulting in materials with a rubber-like behavior [33].

This structural cohesion of the samples cured at 190 °C for 11.5 and 15 min is also reflected in the mechanical properties, yielding high values of tensile strength and elongation at break for both samples. A similar structure is observed in the sample cured at 200 °C for 11.5 min (Fig. 7h). Finally, it can be seen that the surface of the sample cured at 200 °C for 15 min (Fig. 7i) presents some roughness with the presence of small microcracks. This structure may be due to the thermal degradation of the PVC after being subjected to high temperatures and long curing times, resulting in lower mechanical properties and dark surface discoloration. The structure herein reported is quite similar to the microstructure of PVC-DOP resin systems, which is a very typical and effective way of plasticizing this polymer [44].

### 3.4. Migration of PVC plastisols with different curing conditions

Evaluation of plasticizer migration in PVC plastisols is a simple method to validate the optimal curing time and temperature conditions. In Fig. 8, the percentage of migrated plasticizer in n-hexane in the plasticized PVC samples cured at different temperatures and times is shown. The amount of plasticizer migrated in all samples is less than 3 %, which is indicative of a good absorption of the plasticizer by the PVC particles during the gelation stage and of high cohesion of the swollen particles as a result of interactions between PVC and the plasticizer, and fusion of the crystalline segments of PVC, which hinders its migration [35]. However, upon observing Fig. 8, slight differences between the different samples obtained are noticeable. The samples cured at 180 and 190 °C exhibit a similar trend. In both cases, the lowest migration is obtained for the samples cured at 11.5 min, with a migration percentage of 2.1 % for the sample cured at 180 °C and 2.4 % for the sample cured at 190 °C, respectively. Additionally, these migration percentages remain invariable for both curing temperatures in the samples cured at 15 min. This indicates that these samples have achieved greater structural cohesion, which hinders the mobility of the plasticizer and therefore its migration. For shorter curing times, such as 8 min, it is observed that for both temperatures the migration is slightly higher, reaching values of 2.4 % and 2.6 % for the samples cured at 180 °C and 190 °C, respectively. This increased migration can be attributed to the lower structural cohesion achieved and the lower interactions between the PVC and the plasticizer obtained in these samples due to the low temperature and/or curing time, facilitating its migration. On the other hand, it is observed that in the samples cured at 200 °C, the lowest migration occurs for the

plastisol cured at 8 min, and this increases as the curing time increases, with the highest migration reached in the sample cured at 15 min, with a migration percentage of 3.0 %. Although this increase is very slight, it may be due to thermal degradation of the sample [35].

### 3.5. Color properties of PVC plastisols with different curing conditions

Color properties in PVC plastisols are of great importance in determining the curing conditions of the material, as they are sensitive to thermal degradation. When subjected to high temperatures and prolonged curing times, these materials undergo changes in color, acquiring orange/brown tones [37]. Therefore, the visual appearance and colorimetric analysis of PVC plastisol samples can help define the optimal curing temperatures and times and can also be of great use at an industrial level for quality control of the materials obtained. In this case, Fig. 9 shows, in a matrix form, the color appearance of the different PVC plastisols obtained and subjected to different curing temperatures and times. As observed, for milder curing conditions such as samples cured at 180 °C for 8 min and 11.5 min and the sample cured at 190 °C for 8 min, the materials acquire a whitish hue with a high degree of transparency. These samples have lower mechanical properties (tensile strength and elongation at break), indicating a lack of structural cohesion due to incomplete curing of the material resulting from the low temperature and/or short curing time. As the temperature and curing time increase, the plastisol acquires a certain brownish/orange hue with high transparency. This is primarily observed in samples cured at 180 °C for 15 min and at 190 °C for 11.5 and 15 min, where the best mechanical properties are obtained. Therefore, this appearance is indicative of complete curing of the material [21]. Finally, for more aggressive curing conditions, such as a curing temperature of 200 °C, for short curing times, such as 8 min, the sample acquires a slightly darker hue compared to the sample cured at 190 °C for 11.5 min, which is indicative of some thermal degradation of the material. For longer curing times, the samples become progressively darker, with the plastisol cured for 15 min appearing black and completely opaque, which indicates thermal degradation of the material. This is also reflected in lower mechanical properties, as shown earlier.

On the other hand, Table 4 displays the coordinates in the CIELAB colorimetric space for each of the PVC plastisol samples obtained. This table provides quantitative color information, allowing for the evaluation of the curing state (undercured, cured, and overcured) of the different samples obtained. As observed in Table 4, the luminance for all three temperatures decreases as the curing time increases. For samples cured at a temperature of 180 °C, the luminance varies from 46.5 % to 41.9 % for samples cured for 8 and 15 min, respectively. Similarly, for samples cured at 190 °C and 200 °C, the luminance varies from 43.4 % to 35.0 % and from 33.9 % to 25.4 %, respectively, for samples cured for 8 and 15 min, respectively. Across all three temperatures, the decrease in luminance with increasing curing time indicates an increase in coloration due to the curing process.

Furthermore, as the curing temperature increases, the luminance decreases for each curing time, with luminance values dropping below 35.0 % for samples experiencing some thermal degradation. Therefore, low luminance values are indicative of thermal degradation. On the other hand, high luminance values, exceeding 42 %, indicate incomplete curing. In this case, fully cured and non-degraded plastisols, those exhibiting the best mechanical properties, fall within luminance values of 35–42 %.

To complete the colorimetric analysis of the samples, it is necessary to consider the values of  $a^*$  and  $b^*$ , which can help determine the curing degree of the PVC plastisols by relating them to the obtained mechanical properties. It is important to note that  $a^*$  values below 0 tend towards green, while values above 0 tend towards red. On the other hand,  $b^*$  values below 0 tend towards blue, while values above 0 tend towards yellow. Fig. 10 shows the graphical representation of the  $a^*$  and  $b^*$  coordinates of each of the PVC plastisols.

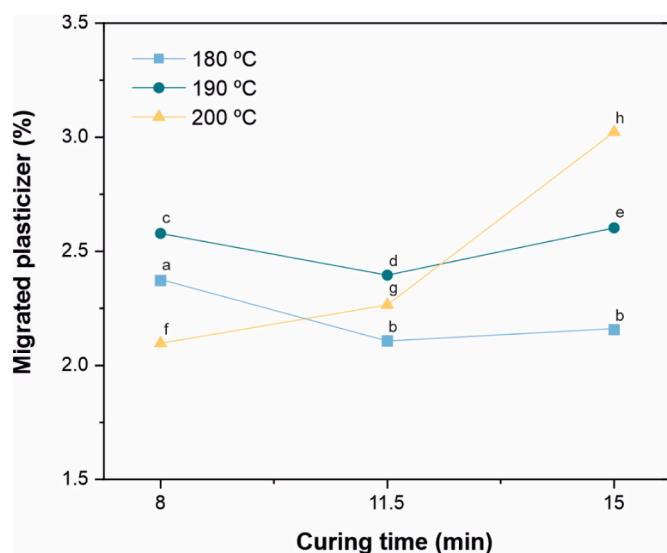


Fig. 8. Plasticizer migration (in weight percentage) of the PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times. <sup>a-h</sup> indicates significant differences between the values obtained ( $p \leq 0.05$ ).



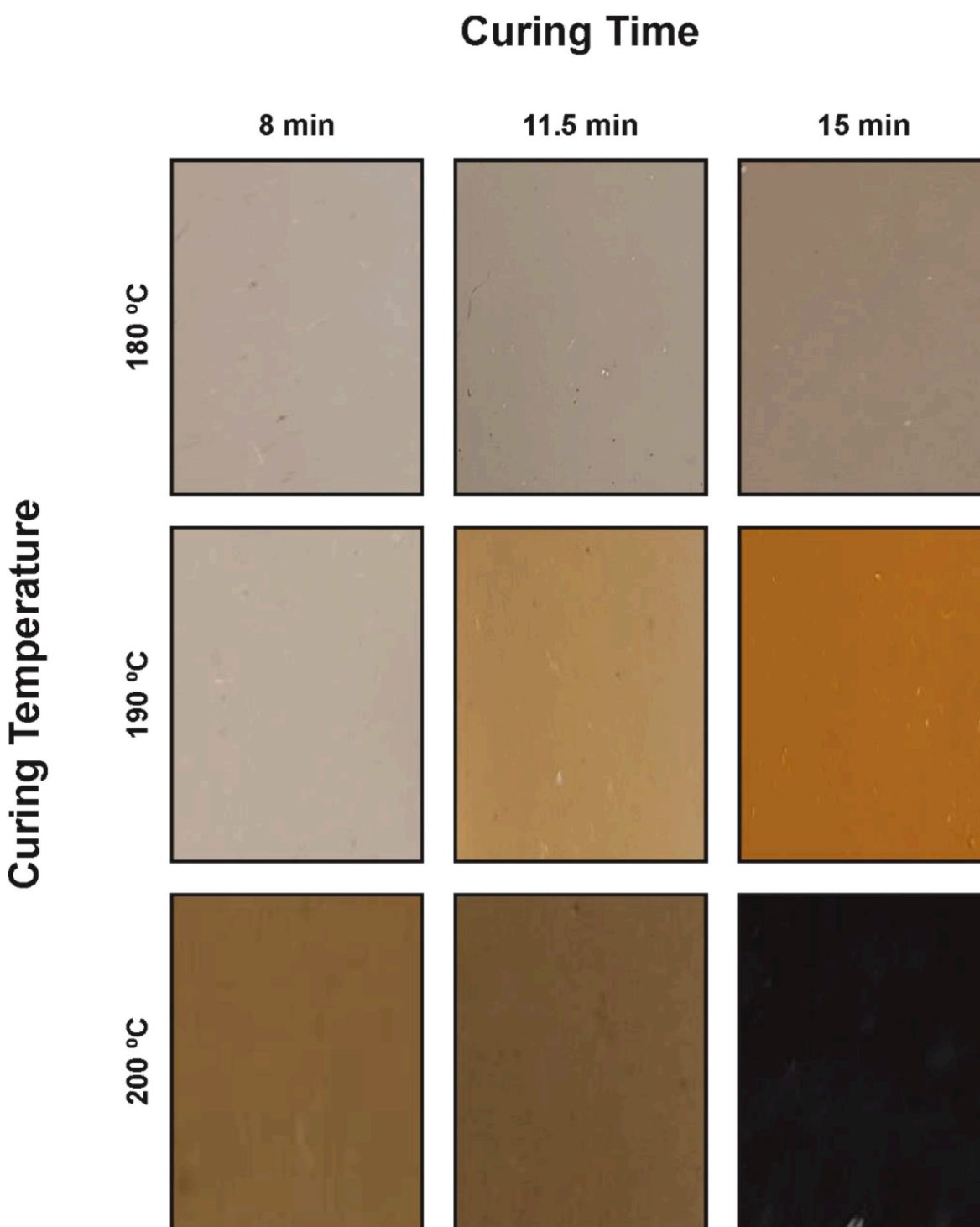


Fig. 9. Visual appearance of the PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.

In this graph, two zones can be distinguished. One zone comprises values of  $a^*$  from 1.3 to 8.3 % and  $b^*$  values from 6.2 to 13.9 %, where the samples have cured properly during the process. Within this zone, two areas can be distinguished: an area (C1) with  $a^*$  values between 1.3 and 2.4 % and  $b^*$  values between 6.8 and 9.8 %, where the samples exhibit partial curing. This corresponds to samples with low mechanical properties because the complete fusion of the PVC crystals did not occur during curing, resulting in a less cohesive structure, likely due to low temperature and/or curing time.

On the other hand, a second area (C2) is observed, where most samples have higher  $a^*$  and  $b^*$  values, ranging from 5 to 8.3 % and

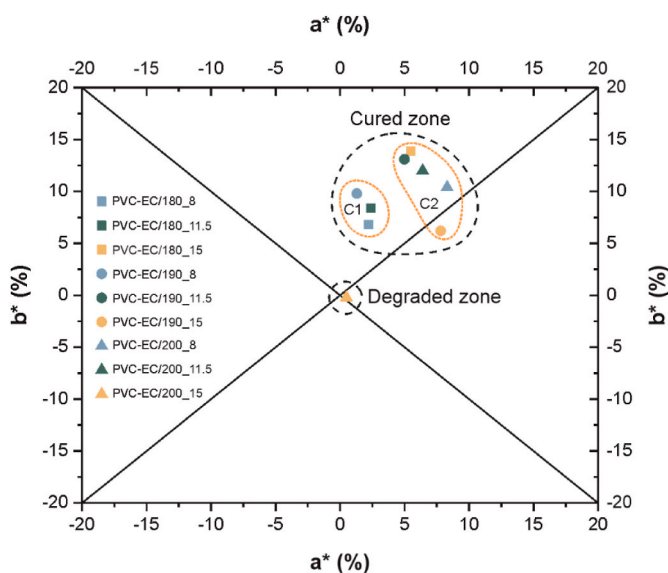
6.2–13.9 %, respectively, indicating an increase in the red and yellow tones of the samples. Samples in this area show higher curing degree and therefore better mechanical properties, primarily due to the increased fusion of PVC microcrystals and hence greater structural cohesion. Finally, it is noted that the  $a^*$  and  $b^*$  coordinates of the sample cured at 200 °C for 15 min decrease compared to the others, approaching 0 % for both coordinates. This, combined with the low luminance obtained in this sample, indicates a brownish coloration, which is indicative of overcuring of the plastisol.

**Table 4**

Luminance ( $L^*$ ) and color coordinates ( $a^*b^*$ ) of the PVC plasticized with ethyl cinnamate under different temperatures and curing times.

Sample	$L^*$	$a^*$	$b^*$
PVC-EC/180_8	46.5 ± 1.0 <sup>a</sup>	2.2 ± 0.3 <sup>a</sup>	6.8 ± 0.6 <sup>a</sup>
PVC-EC/180_11.5	42.4 ± 0.6 <sup>b</sup>	2.4 ± 0.3 <sup>a</sup>	8.4 ± 0.4 <sup>b</sup>
PVC-EC/180_15	41.9 ± 0.1 <sup>b</sup>	5.5 ± 0.2 <sup>b</sup>	13.9 ± 0.4 <sup>c</sup>
PVC-EC/190_8	43.4 ± 1.2 <sup>b</sup>	1.3 ± 0.1 <sup>c</sup>	9.8 ± 0.3 <sup>d</sup>
PVC-EC/190_11.5	40.9 ± 0.6 <sup>c</sup>	5.0 ± 0.6 <sup>d</sup>	13.1 ± 0.7 <sup>f</sup>
PVC-EC/190_15	35.0 ± 0.4 <sup>d</sup>	7.8 ± 0.5 <sup>e</sup>	6.2 ± 0.5 <sup>g</sup>
PVC-EC/200_8	33.9 ± 0.5 <sup>e</sup>	8.3 ± 0.5 <sup>f</sup>	10.4 ± 0.4 <sup>h</sup>
PVC-EC/200_11.5	33.8 ± 0.8 <sup>e</sup>	6.4 ± 0.3 <sup>g</sup>	12.0 ± 0.7 <sup>i</sup>
PVC-EC/200_15	25.4 ± 0.2 <sup>f</sup>	0.5 ± 0.1 <sup>h</sup>	-0.2 ± 0.1 <sup>j</sup>

<sup>a-j</sup> indicates significant differences between the values obtained ( $p \leq 0.05$ ).



**Fig. 10.** Variation of the color coordinates  $a^*$  and  $b^*$  of the PVC plastisols plasticized with ethyl cinnamate under different temperatures and curing times.

#### 4. Conclusions

The optimization of curing conditions for PVC plastisols plasticized with 70 phr of ethyl cinnamate, a bio-based plasticizer with significant potential in polymer plasticization, was conducted. Among the investigated conditions, optimal material properties were achieved at a curing temperature of 190 °C for 11.5 min. Under these curing conditions, a tensile strength of 6.4 MPa and a high elongation at break of approximately 570 % were obtained, surpassing those of other bio-based plasticizers, highlighting the potential of ethyl cinnamate for flexible PVC production. Furthermore, scanning electron microscopy (FESEM) revealed a smooth and homogeneous microstructure for samples cured under these conditions, indicative of complete curing with the fusion of PVC microcrystals and enhanced structural cross-linking, resulting in a fully cohesive material with good mechanical properties. This structural cohesion was confirmed by thermogravimetry, which showed higher PVC dehydrochlorination temperatures for samples with better mechanical properties, particularly evident in samples cured at 190 °C for 11.5 min. Moreover, a relationship between curing conditions and plasticizer migration was observed, with samples exhibiting better mechanical properties showing lower migration due to increased structural cohesion hindering plasticizer mobility. However, it is noteworthy that the migration observed in all samples was below 3 wt%. Finally, visual appearance and color properties of the obtained plastisols under different curing conditions were analyzed, providing a simple means to validate the effectiveness of the curing process and detect material

degradation, as PVC is highly sensitive to temperature. It was observed that materials cured at high temperatures (200 °C) experienced some thermal degradation, resulting in lower mechanical properties.

All in all, the use of ethyl cinnamate as a bio-based PVC plasticizer emerges as an interesting and viable alternative to traditional industrial plasticizers for plastisol production. This study demonstrates the possibility of obtaining plastisols with high environmental efficiency, excellent ductile properties, and low migration using ethyl cinnamate as a plasticizer.

#### CRedit authorship contribution statement

**J. Gomez-Caturla:** Writing – original draft, Investigation, Data curation. **M. Miranda-Pinzon:** Methodology, Investigation, Formal analysis. **M.P. Arrieta:** Writing – review & editing, Visualization, Supervision. **L. Quiles-Carrillo:** Project administration, Formal analysis, Data curation. **D. Garcia-Garcia:** Supervision, Resources, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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