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The effect of the curing time and temperature on final properties of flexible PVC with an epoxidized fatty acid ester as natural-based plasticizer

O. Fenollar · L. Sanchez-Nacher · D. Garcia-Sanoguera · J. López · R. Balart

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Abstract One of the most useful polymeric materials at industrial scale is plasticized polyvinyl chloride (P-PVC) or PVC plastisol. This is characterized by optimum balance among processing conditions, overall properties, cost, and versatility; however, it has some problems related to plasticizer migration (generally phthalates derivatives) with toxicity problems. As a consequence of the appearance of new regulations which restrict the use of phthalates, the study of new plasticizers with low toxicity and low migration has become a very interesting research field. In this study, the optimum curing conditions of vinyl plastisols with a natural-based epoxidized fatty acid ester as plasticizer have been investigated by the following mechanical properties: thermal behavior, color changes, solvent migration, and microstructure changes in terms of the curing conditions. This study was carried out with a plasticizer content of 70 phr (per hundred resin); different isothermal curing conditions ranging from 160 to 220 °C, and curing times in the 6–10 min range were used. The results revealed that the best curing conditions are 200 and 220 °C for curing times near to 14 and 10 min, respectively, which are similar to those used for other commonly used plasticizers.

Introduction

Flexible or plasticized polyvinyl chloride (P-PVC) is a widely used material in several industrial sectors such as packaging, toys, biomedicine, building, and so on. This kind of flexible PVC is characterized by the use of plasticizers (low-molecular-weight compounds) to achieve flexibility. The most extended plasticizers at industrial scale are based on phthalates formulations, such as bis(2-ethyhexyl) phthalate (DEHP) and especially di-"isononyl" phthalate (DINP). However, many of the traditional plasticizers show an important migration phenomenon toward contact elements and this could cause some toxicity problems [1, 2]. Therefore, the use of these plasticizers is being questioned by their possible toxicity problems related to phthalates' migration [3–5]. This fact has promoted some countries to develop new and restrictive regulations about phthalates uses in flexible PVC products. The European Parliament and the Council developed a new directive (2005/84/EC) in 2005 regarding to restrictions on the marketing and use of several phthalates in toys and childcare articles. These restrictions affected six phthalates derivatives: DEHP, dibutyl phthalate, benzyl butyl phthalate, DINP, di-"isodecyl" phthalate, and di-*n*-octyl phthalate [6]. In a similar way, other countries have developed similar normative regarding the use of phthalates for applications with possible contact with children. In the case of the United States of America, on February 2009, a new regulation (public law 110–314—August 14, 2008) which limits the use of the abovementioned phthalates in children's products has gone into effect. Both European and American regulations define the maximum amount of these phthalates at concentrations lower than 0.1 wt% [7]. To solve this real problem, alternative plasticizers and mixtures, with low migration levels and low toxicity have been widely used in the last decades. These alternative plasticizers could be very useful for applications which are especially sensitive to this phenomenon [8, 9]. For all these reasons, other plasticizers such as citrates, benzoates, carboxylates, and so on have

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O. Fenollar · L. Sanchez-Nacher · D. Garcia-Sanoguera (✉) · J. López · R. Balart
Materials Technology Institute (ITM), Polytechnic University of Valencia, Plaza Ferrándiz y Carbonell s/n, Alcoy 03801, Alicante, Spain
e-mail: dagarsa@dimm.upv.es

been proposed as alternative materials for PVC plasticization. This plasticizer group offers interesting possibilities for real industrial applications because they can be processed in a similar way to phthalate-based PVC formulations and also offer similar overall properties [10, 11]. Nowadays, there is an increasing interest on the use of natural-based plasticizers which are characterized by low toxicity and low migration. This group includes epoxidized triglyceride vegetable oils coming from soybean oil, linseed oil, castor-oil, sunflower oil, and fatty acid esters (FAEs) [12–15]. Although research on these epoxidized compounds has been reported since the 1960s decade, the interest on the use of these compounds as alternative plasticizer has increased in a remarkable way as a consequence of current regulation on phthalates and derivatives [16]. Epoxidized oils show excellent heat and light stability as a consequence of the presence of oxyrane groups. Nevertheless some problems related to compatibility of epoxidized oils with PVC resins have been reported, so important efforts have been focused on oil esterification and subsequent epoxidation in order to increase interactions [17, 18]. Fatty epoxides are highly compatible with PVC resins and can increase thermal stability of the plasticized compounds [19]. These plasticizers are classified as secondary plasticizers because they can exert two effects. They act as internal lubricant and thermal stabilizers due to the presence of epoxide groups that are capable to scavenge acid groups through catalytic degradation, thus having a positive effect on overall stabilization [20–23].

To evaluate the possibilities of replacing traditional plasticizers with natural-based plasticizers, it is important to perform a complete study of the curing process in order to optimize the final properties which are directly related to the curing conditions.

A PVC plastisol is a mixture of fine particles and aggregates of a PVC resin in a liquid dispersion of a plasticizer. As the plastisol is heated, the plasticizer enters inside the aggregate voids and forms a homogeneous paste. Above the PVC glass transition temperature, some PVC particles begin to absorb plasticizer and then the plastisol becomes a solid paste (this process is named gelation); nevertheless, it has not still reached enough particle cohesion, so that mechanical properties are poor [24, 25]. It is necessary to reach temperatures more than 190 °C to achieve the melting of PVC microcrystallites to form a homogeneous and uniform matrix. After a cooling process, the internal structure is like a rubbery solid with optimum mechanical strength [26]. Usually, the industrial curing process of these polymeric materials is carried out at isothermal conditions. The main parameters to determine this process are curing temperature and curing time.

In this research, we have worked with plasticized PVC formulations based on the use of a natural-based plasticizer derived from an epoxidized fatty acid ester (EFAE) octyl epoxyoleate. The plasticizer content was fixed to 70 phr (per hundred resin) which is similar to other industrial formulations. We have studied the optimum curing conditions in terms of temperature and time to determine the possibilities of replacing traditional plasticizers. In this study, we have analyzed the variation of mechanical properties, microstructure, coloration, and migration levels of PVC plastisol with this natural-based plasticizer. The obtained results show similar curing conditions to many industrial plasticizers as well as balanced overall properties.

Experimental

Materials and procedures

The PVC resin Lacovyl PB 1172 H was supplied by Atofina UK Ltd., Midlands, UK, with a *K* value of 67 obtained by ISO 1628-2. As natural-based plasticizer, an epoxyester fatty acid (EFAE, octyl epoxyoleate C_{25} H_{50} O_3, CAS number 106-84-3) commercial grade 401 with an average molecular weight of 546 g mol^{-1} supplied by Traquisa S.A., Madrid, Spain, was used. Table 1 shows a summary with the main characteristics of this plasticizer.

Plastisol preparation

All plastisols were prepared by mixing 70 phr of plasticizer with PVC resin in a rotative mixer KAPL mod. 5KPMS (KAPL, MI, USA) for 10 min at a rotating speed of 3 rpm. After the mixing process, the pastes were subjected to a vacuum process for 15 min in an MCP Group vacuum chamber model 00ILC (HEK-GmbH, Lubeck, Germany) with a maximum vacuum of −1 bar. Once all air bubbles were removed, plastisols were spread into an aluminum mold.

Table 1 Main characteristics of plasticizer 401 based on fatty acid epoxyester structure (EFAE)

Density at 20 °C (g cm^{-3})	0.92 ± 0.01
Viscosity at 20 °C (cp)	45–55
Acid index (mg KOH g^{-1})	≤1
Refraction index at 16 °C	1.4605–1.4610
Iode index	≤3
Gardner color	≤2
Inflammation point (°C)	>200
Epoxide oxygen (%)	4.5–5
Freeze temperature (°C)	−18
Water solubility (g L^{-1})	Non-soluble
Aspect at room temperature	Olious liquid

The curing process of the plastisol was performed in a ventilated oven Carbolite mod. 2416CG (Keison Products, Barcelona, Spain) with a maximum temperature of 300 °C. The curing process was carried out at several isothermal temperatures ranging from 160 to 220 °C and the curing time varied in the 6–16 min range.

Sheets 190 × 125 × 5 mm^3 in size were obtained after the curing process in an aluminum mold. These sheets were stamped in a die on a hydraulic press mod. MEGA KCK-15A (Melchor Gabilondo S.A., Vizcaya, Spain) to obtain standardized samples for mechanical characterization.

Mechanical characterization

Mechanical characterization was carried out using a universal tensile test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain) following ISO 527. A 20 mm min^{-1} crosshead speed was used to obtain the tensile graph with a load cell of 5 kN. All specimens were tested at room temperature; a minimum of five samples were analyzed and average values of tensile strength and elongation at break were calculated.

Microscopic characterization

Morphology analysis of tensile fractured surfaces of plastisols was carried out by means of a scanning electron microscope JEOL JSM-6300 (Jeol USA, Peabody) using secondary electrons with an acceleration voltage of 15 kV. Samples were covered with Au layer (5–7 nm) by sputtering in vacuum conditions prior to each measurement.

Color measurements

Color coordinates were measured with a Hunter spectrophotometer Mod. CFLX-DIFF-2 (Hunterlab, Murnau, Germany). This allows measurements with different color scales (CIE, XYZ, Hunterlab CIE $L^*a^*b^*$) and also provides different color indexes as well as spectral data from 400 to 700 nm at a step of 10 nm. This spectrophotometer is useful for both opaque and translucent materials such as PVC plastisols.

Thermal characterization

The calorimetric analysis was carried out using a DSC Mettler-Toledo 821 equipment (Mettler-Toledo, Schwerzenbach, Switzerland). Samples ranging between 4 and 6 mg in weight were used. A first cooling from 25 to −55 °C at a cooling rate of −5 °C min^{-1} was completed since the main thermal transitions are below room temperature; after this, a heating process from −55 up to 25 °C at 5 °C min^{-1} was carried out. All thermal transitions were determined from the second heating process. Tests were performed in an air atmosphere.

Migration tests

Migration tests were carried in *n*-hexane. This is an extraction/gravimetric method in which samples are immersed in *n*-hexane at a constant temperature of 50 °C, and after 2 h the weight loss is measured. This method considers that the weight of the residue extract presented in *n*-hexane is equal to the plasticizer extracted from the sample.

Results and discussion

Influence of curing temperature and time on mechanical properties

In this study, we followed a typical methodology of industrial processing, and we focused on the curing conditions commonly used at industrial scale. The optimum curing conditions of vinyl plastisols require a balance between two main parameters: temperature and curing time; it is absolutely necessary to select an appropriate temperature and curing time to ensure a complete curing process because it is the key factor to obtain good mechanical properties with industrially advantageous conditions.

Figure 1 shows the plot evolution of the tensile strength as a function of curing time for PVC/EFAE plasticizer system cured at different isothermal temperatures. As it can be observed, the tensile strength exhibits a marked upward tendency with curing time and temperature. The effects of the curing process can easily be observed by following the

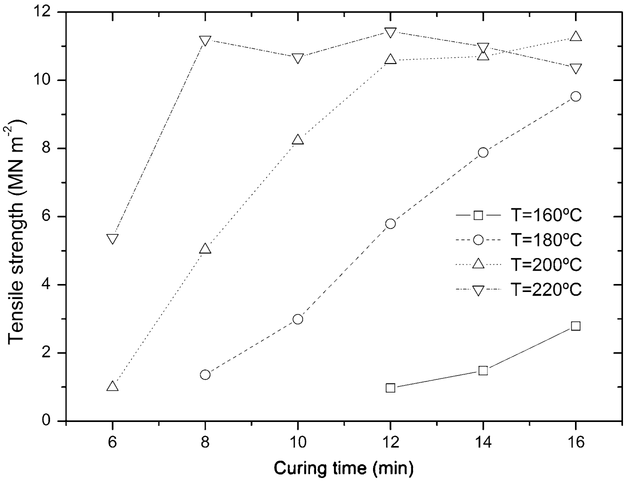

Fig. 1 Variation of tensile strength of vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at different temperatures in terms of the curing time

tensile strength analysis. This is because tensile strength is very sensitive to the degree of curing. If the material is not fully cured, it has not enough consistency and this leads to early breakage. However when the plastisol is completely cured, its tensile strength increases up to maximum values due to the high cohesion level reached between PVC particles and absorbed plasticizer. At low curing temperatures, 160 °C, we can see that tensile strength values are very low. For times less than 12 min, the material breaks easily. Higher curing times lead to a slight increase in tensile strength, from 0.9 to 2.8 MPa for curing times of 12 and 16 min, respectively. This indicates that the curing process has not been completed and then plastisol remains as a solid paste mechanical properties are still poor. As we have described before, to completely cure a plastisol, it is necessary to reach temperatures over 180–190 °C to promote fusion of microcrystallites. If the plastisol is isothermally cured at 180 °C, the curing process is rapidly completed as it can be observed in Fig. 1. Tensile strength value varies from 1.3 to 9.5 MPa for curing times of 8 and 16 min, respectively.

When plastisol is cured at an isothermal temperature of 200 °C, we also observe a remarkable increase in tensile strength values from 1.0 MPa for short curing times (around 6 min), up to 10.7 and 11.26 MPa for curing times of 10 and 12 min, respectively. An increase in the curing time does not promote significant changes in tensile strength; however, it is important to take into account that an excessive exposure of the plastisol to high temperatures may induce degradation processes since PVC is especially sensitive to thermal degradation [27]. When PVC plastisol is isothermally cured at 220 °C, the process is fully completed with relatively short times; although the temperature is high we need some times to ensure optimum PVC particles swelling in order to achieve maximum particle cohesion (interaction); for this reason with curing times more than 12 min this plastisol reaches tensile strength values of about 11.4 MPa. Moreover, for these times and temperatures, degradation process becomes at the same time that curing process and this could have a negative effect on material performance due to thermal degradation [28]. It is important to consider that DEHP-based plastisols with a plasticizer content of 70 phr show a tensile strength of about 12 MPa (isothermally cured at 200 °C and 9 min) which is similar to the values obtained for PVC/EFAE system. Another PVC–plasticizer system which is widely used at industrial scale is based on the use of DINP. This system shows a tensile slightly higher (about 14 MPa) for the same curing conditions and composition as described before [29]. Thus, we can observe that the use of similar processing conditions lead to similar tensile strength values.

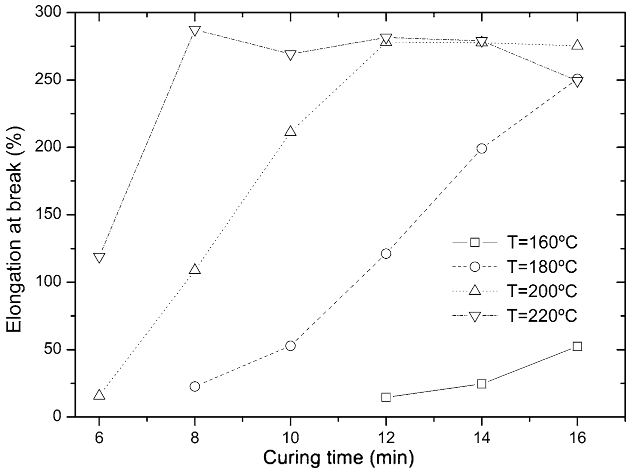

Fig. 2 Variation of elongation at break of vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at different temperatures in terms of the curing time

Other parameter, highly sensitive to curing degree, is the elongation at break as a ductile property. Figure 2 shows the variation of elongation at break in terms of the curing time for several isothermal curing temperatures. As the curing process occurs, particle cohesion increases and, consequently, elongation at break is better because the plasticization effect is optimum.

For low curing temperatures, around 160 °C, elongation at break reaches values around 52% for a curing time of 16 min. This value is representative for incomplete curing process; it has not reached enough particle cohesion between swollen particles to transfer the stresses in an appropriate way and, because of this, the material shows poor ductile properties. If plastisols are isothermally cured at 180 °C, elongation at break is good for long curing times (16 min), but this is too long for industrial processing. The use of temperatures around 200 °C allows reaching the best elongation at break values, 277%, for curing times of 12 min. If we use longer curing times, there are no important changes in elongation at break (it is probably because plastisol has become more fragile as a consequence of thermal degradation). When the plastisol is isothermally cured at 220 °C, the maximum values for elongation at break (287%) for 8 min is obtained; if the curing time is increased, we observe a decrease in elongation at break due to thermal degradation. PVC plastisols based on the use of DEHP or DINP reach elongation at break values in the 400–420% range for a plasticizer amount of 70 phr (cured at 200 °C and 9 min). This is related to plasticizer structure and molecular weight. DEHP and DINP have an average molecular weight of 390.54 and 420.6 g mol^{-1}, respectively, whereas EFAE molecular weight is 546 g mol^{-1}. Molecular weight is directly related to chain mobility, so that high-molecular-weight results in lower mobility and this could lead to low elongation at break values in the PVC/EFAE system. Despite this, elongation at break of the PVC/EFAE system is high enough to obtain flexible materials.

Influence of curing temperature and time on plastisol structure

The effects of the curing temperature and time as the main processing parameters in PVC/EFAE system can be observed through surface analysis of fractured materials since fracture is directly related to particle cohesion. Figures 3, 4 and 5 show fractured surfaces (magnification 1000×) corresponding to samples isothermally cured at different conditions. It is important to remark that the gelation/curing process takes place through different stages [30]. In the first stage, plasticizer enters inside cavities of some PVC aggregates thus leading to particle swelling. The spherical particles grow and stay together; at this stage the material seems a solid, but it has not enough mechanical strength (it has a solid paste consistency) [31, 32]. This stage is microstructurally characterized by swollen spherical particles and aggregates. In a second stage, the swelling process continues as temperature increases. In these conditions, the vinyl plastisol reaches some mechanical properties, but it is necessary to increase temperature and curing time to achieve complete curing. Over 180–190 °C, microcrystalline regions of PVC fuse and form a homogeneous structure. After this stage the curing process has been completed and subsequent cooling will lead to the optimum mechanical properties. Figure 3 shows SEM microphotographs of fractured surfaces of the PVC–EFAE system isothermally cured at 180 °C for different times. For short curing times (6 min) it can be observed the presence of aggregates and individual PVC spherical particles (Fig. 3a). Figure 3b, c shows a heterogeneous morphology (even for longer curing times) because the gelation process does not take place within these curing conditions; only some plasticizer absorption can be detected [33]. These materials have very poor mechanical properties as a consequence of low particle cohesion as described before.

Figure 4 shows SEM microphotographs of fractured samples isothermally cured at 200 °C for different times. Figure 4a (curing time of 6 min) shows the presence of PVC swollen particles and aggregates as a consequence of plasticizer absorption. In Fig. 4b, with a curing time of 10 min, it can be observed a similar morphology, which is characterized by the presence of spherical particles and aggregates with apparently more strong fracture conditions. This phenomenon indicates that the melting process has started; because of this, mechanical strength is higher, although gelation process has not been completed yet. This situation can also be seen in Fig. 4c; for a long curing time (14 min), the morphology formed shows a regular and homogeneous appearance, with some dispersed and localized individual particles. This fact indicates an almost completed curing process which is responsible for higher mechanical properties.

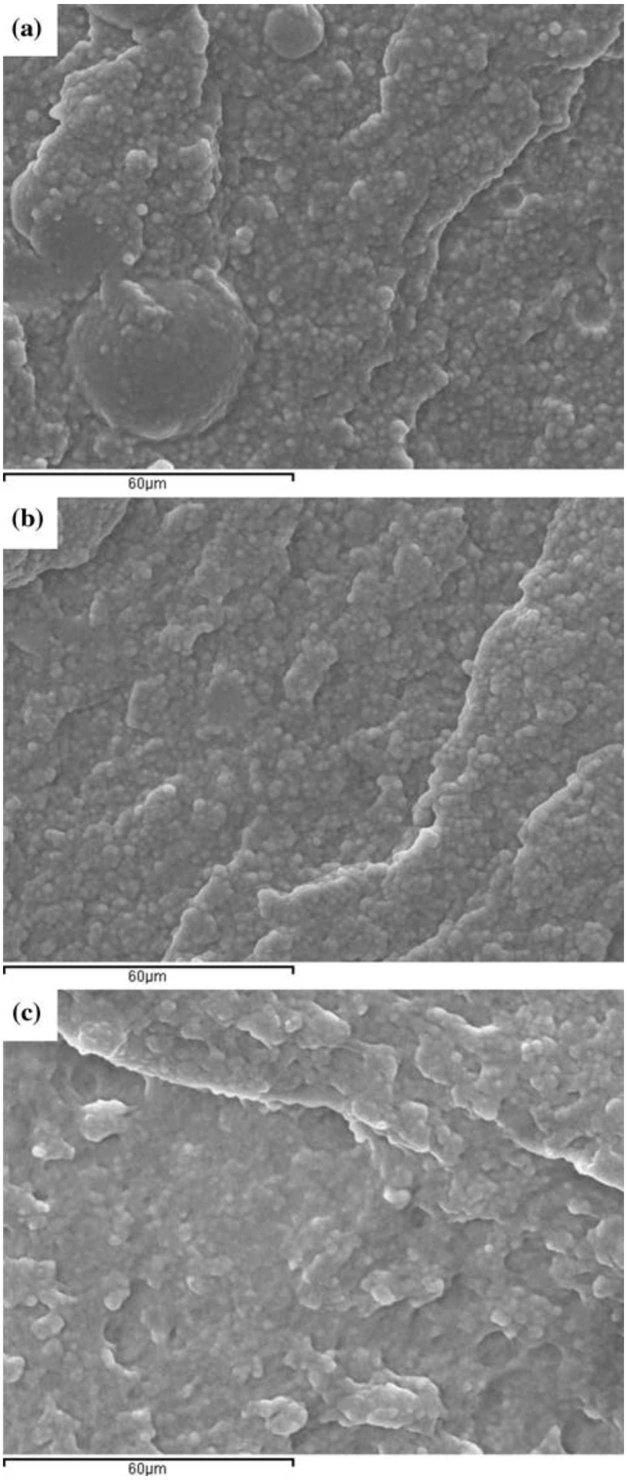

Fig. 3 SEM microphotographs (1000×) of fractured surfaces of vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at 180 °C for different curing times: **a** $t = 6$ min, **b** $t = 10$ min, **c** $t = 14$ min

SEM microphotograph analysis for plastisols isothermally cured at 220 °C at different times allows the observation of the different stages during the gelation and curing

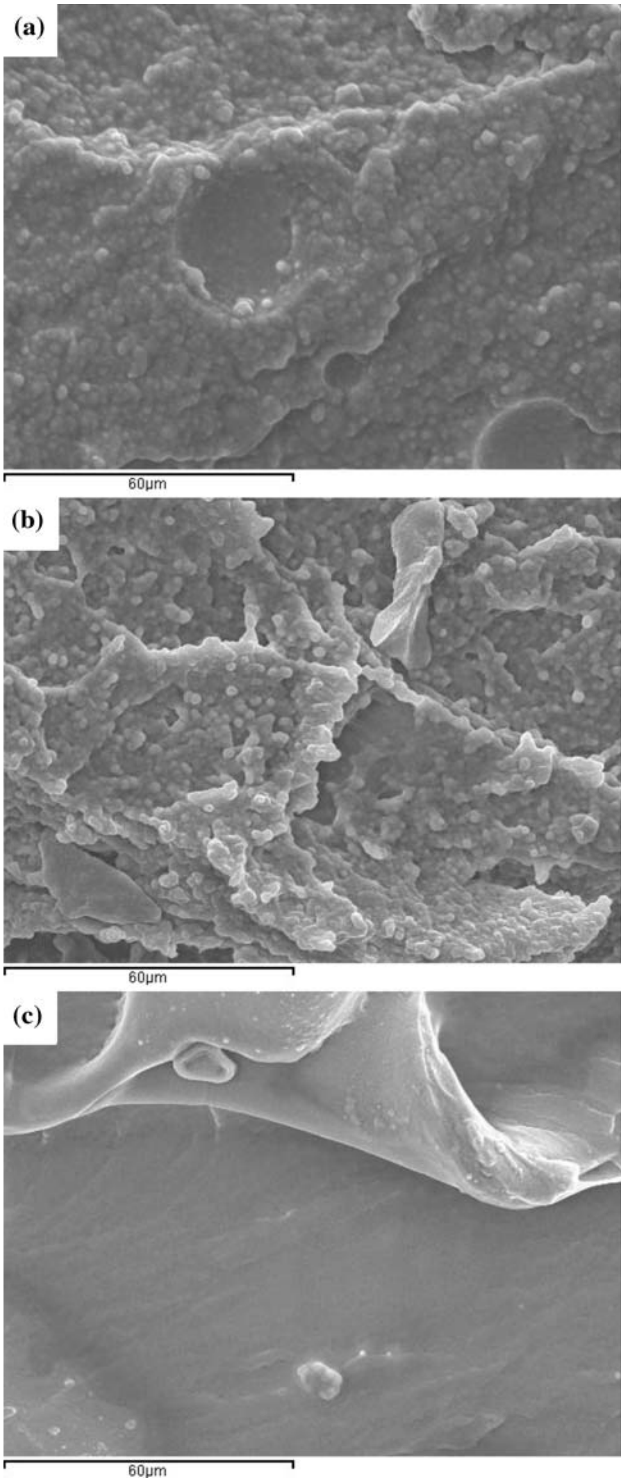

Fig. 4 SEM microphotographs (1000×) of fractured surfaces of vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at 200 °C for different curing times: **a** $t = 6$ min, **b** $t = 10$ min, **c** $t = 14$ min

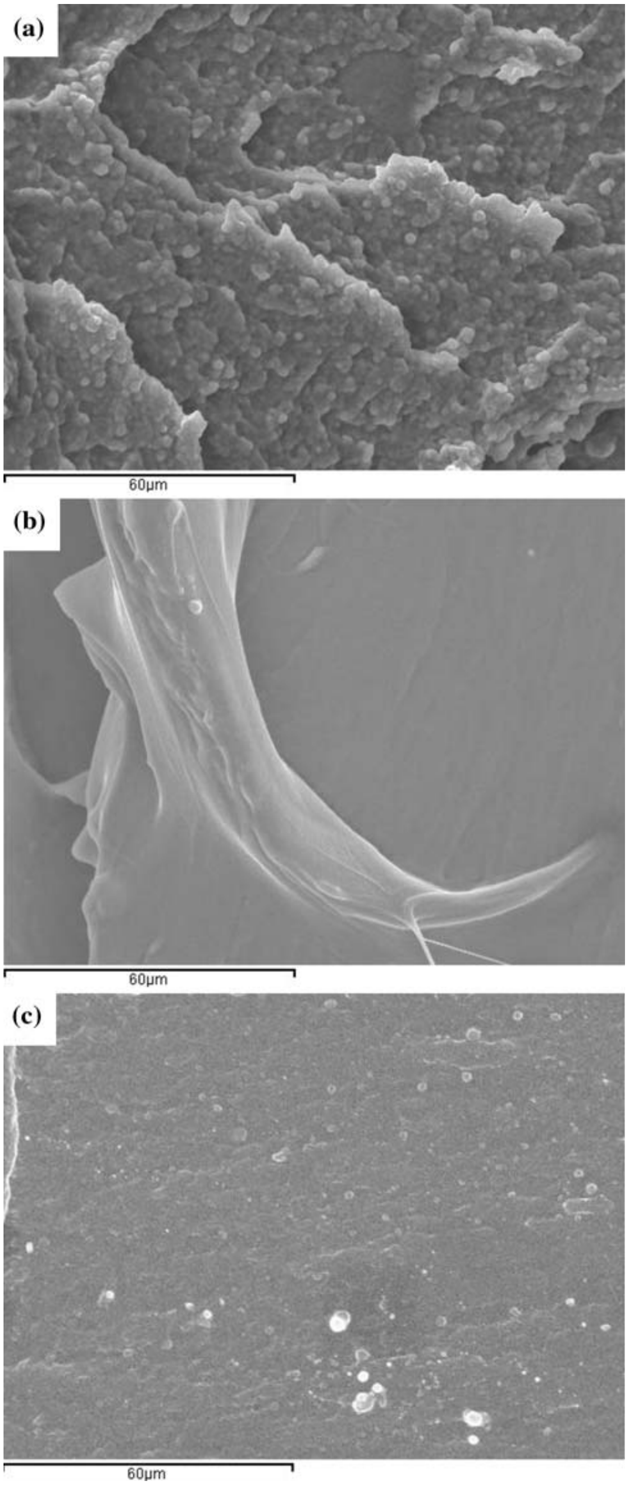

Fig. 5 SEM microphotographs (1000×) of fractured surfaces of vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at 220 °C for different curing times: **a** $t = 6$ min, **b** $t = 10$ min, **c** $t = 14$ min

processes as described before. For low curing time (Fig. 5a), an internal structure with spherical PVC particles can be detected. These particles form some aggregates thus indicating that the plasticizer has entered some voids and cavities. In Fig. 5b it can be observed that for longer times (10 min), a homogeneous structure is obtained thus indicating that the crystalline phase has fused. This surface morphology shows evidences of elastic and plastic deformation such as waves and threads formed during the deformation-fracture process. Also, with these curing conditions, mechanical properties are increase in a remarkable way as a consequence of particle cohesion. Figure 5c shows the fractured surface of a PVC/EFAE system isothermally cured at 220 °C and 14 min curing time. As it can be observed, it shows a different morphology than the previous one, because this belongs to degraded plastisol. The material behavior is brittle, becomes rigid and some microcracks and little discontinuities appear on the surface due to thermal degradation.

Influence of curing temperature and time on plastisol color

The effects of the curing conditions can also be studied by color measurements. In a qualitative way, we can observe white and opaque surfaces on samples cured at low temperatures and short curing times; this is representative for partial plasticizer absorption. As the gelation-curing process takes place, samples acquire yellowish coloration and simultaneously, transparency is achieved. This yellowish appearance is representative for good plasticizer absorption as a consequence of the natural color of the fatty acid epoxyester plasticizer (slightly yellow). If the plastisol is subjected to high temperatures and long curing times, surface color changes to a dark brown coloration with some transparency. Thus we can establish a direct relationship between color changes of a plastisol and the curing degree.

For this reason, the colorimetric study is a complementary technique that permits quantify the color variations on vinyl plastisols to define the optimum curing times and temperatures; furthermore, due to its simplicity and low cost of the equipment, it is an interesting method to perform a quality control of the curing process at industrial scale.

Colorimetric study allows obtaining more quantitative information about the curing process by following the evolution of several color coordinates: a^*, b^* ($a^* > 0$ tends to magenta and $a^* < 0$ tends to green; $b^* > 0$ tends to yellow and $b^* < 0$ tends to blue). Figure 6 shows variation of color coordinates a^* and b^* for PVC/EFAE system isothermally cured at different temperatures and different curing times. As we have indicated previously, non-cured (or partially cured) plastisols are characterized by whiteness coloring and opacity. Plastisols isothermally cured at 160 °C and different times in 8–16 min range, show very low a^* coordinate values (all of them negatives), and b^* values around 5%. Samples isothermally cured at 180 °C and short times show the same effect, but as the curing time increases (14 and 16 min), b^* values increase up to values around 10% while a^* is negative yet. All these values correspond to white and opaque appearance (see zone Z_1 in Fig. 6). If plastisols are isothermally cured at 180 °C the curing process takes place in a great extent, and plastisol samples acquire a slight yellow color and some transparency as a consequence of the intrinsic color of the fatty acid epoxyester plasticizer (see zone Z_2 in Fig. 6). The use of a curing temperature of 200 °C is characterized by negative a^* values and b^* values around 5%, with short curing time. For longer curing times, both a^* and b^* color coordinates increase (a^* up to 14.3% and b^* up to 19.5%). This variation goes through zone Z_1 (non-cured plastisol with whiteness appearance), zone Z_2 (partially cured plastisol with yellow appearance), and zone Z_3 (b^* values upper than 15% and a^* values upper than 9%) characterized by an increase in the yellow color toward darkness ones. If plastisols are isothermally cured at 220 °C the color coordinates rapidly evolve through Z_1, Z_2, and Z_3 zones and a new zone Z_4 is detected which is characterized by a combination of a^* values (ranged from 12 to 4%) with b^* values (ranged from 6 to 0%) that tend to magenta with a brownish appearance; this is representative for plastisol thermal degradation state.

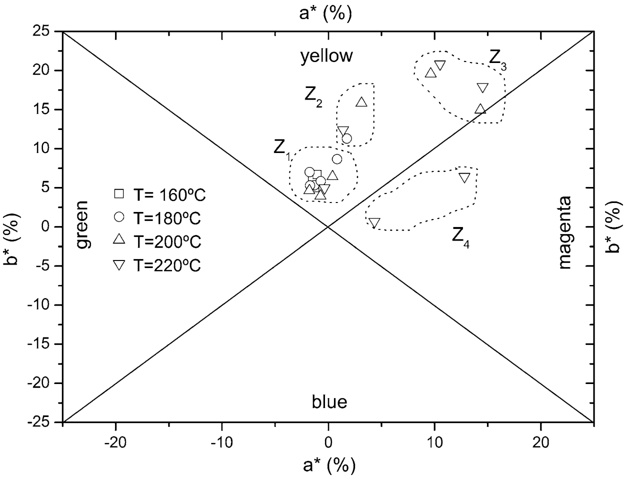

Fig. 6 Variation of a^* and b^* color coordinates for vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at different temperatures in terms of the curing time

On the other hand, Fig. 7 shows the evolution of the luminance (L^*) for plastisols isothermally cured at different temperatures and different curing times. We have to take into account that L^* is the amount of reflected light. For low curing temperatures (160 °C), we can see that luminance values decrease from 88 to 55% for curing times between 8 and 16 min, respectively. At higher curing temperatures (180 °C), L^* values vary from 86 to 37% for curing times of 6 and 16 min, respectively; for both series the main characteristic is the white and opaque appearance that indicates that curing process is not complete (like zone Z_1 observed previously in Fig. 6).

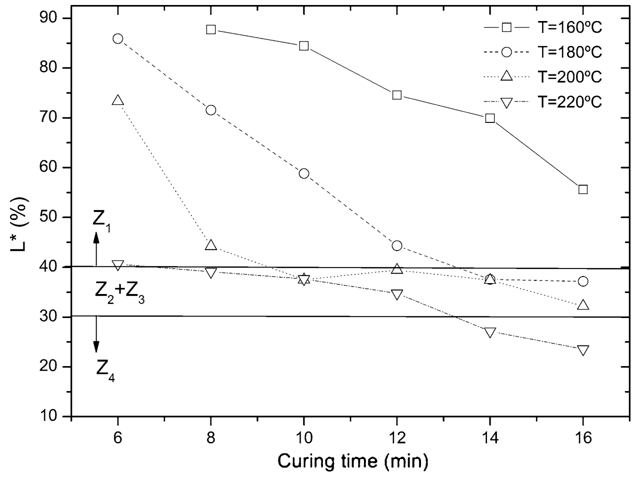

Fig. 7 Variation of luminance *L** for vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at different temperatures in terms of the curing time

If plastisols are isothermally cured at 200 °C we also observe a decrease in luminance, from 73% for short curing times around 6 min up to 32% for curing times of about 16 min. When vinyl plastisol are isothermally cured at 220 °C, *L** values are in the 40–23% range for the same curing times. For these higher temperatures, *L** values around 40% indicate good curing conditions with typical yellowish coloration and transparency; luminance values over 40% are representative for poor cured conditions so gelation process is not completed (zone Z_2 and Z_3); for long curing times, luminance decreases and reaches values <35% and this corresponds to brownish coloration (zone Z_4). For these curing conditions, degradation processes take place. It is important to remark that the excessive exposure of the plastisol to high temperatures and curing times may induce degradation processes because PVC is especially sensitive to thermal degradation. Similar evolution can be observed in PVC/DEHP and PVC/DINP systems so color measurement is a simple method to perform a quality control of the curing process in order to obtain the optimum overall properties which are accomplished with the optimum balance between curing time and temperature [34].

Influence of curing temperature on plastisol thermal characterization

Thermal characterization was carried out in order to complete the study of gelation and curing processes because the calorimetric analysis evidences important differences in vinyl plastisol samples cured at different conditions. Figure 8 shows the calorimetric curves of individual PVC resin and EFAE plasticizer; the glass transition of PVC is located at 85.0 °C, and the plasticizer shows a melting point at about –16.9 °C. PVC/EFAE plastisols isothermally cured at 160 °C show a characteristic DSC curve; we observe an endothermic peak located in the −17.4 to −18.4 °C range, corresponding to short curing time (8–10 min range). This peak indicates the presence of free plasticizer that has not been absorbed yet by PVC particles and aggregates. If we take into account the heat of fusion of the plasticizer which is around 92 J g^{-1} (obtained by DSC analysis) it is possible to estimate in a simple way the amount of free plasticizer that has not been absorbed by PVC particles. A thermal characterization summary of the PVC/EFAE system isothermally cured at different temperatures and times is showed in Table 2.

The normalized values of the peak integral for samples isothermally cured at 160 °C give percentages of free plasticizer close to 11.7 and 7.2% for curing times of 8 and 10 min, respectively. For curing temperatures of 180 °C we can observe only one peak that corresponds to short curing time (8 min) and this one represents 8% of free plasticizer. For long curing times at this temperature we do not observe any endothermic peak corresponding to free plasticizer and this indicates total absorption of plasticizer by PVC particles and aggregates. For samples isothermally cured at 200 and 220 °C, no endothermic peak related to the presence of free plasticizer is observed, even for short curing times. Despite total plasticizer absorption is detected by DSC analysis, a minimum curing time is needed in order to ensure good mechanical properties.

Influence of curing temperature and time on plasticizer migration

Finally we have used a migration study to validate the optimum curing conditions obtained in previous experiences. Figure 9 shows a plot evolution of plasticizer migration in *n*-hexane as a function of curing parameters. It is interesting to remark that for 160 °C the plasticizer migration values are the highest, between 34 and 7.5%. As it has been described previously, with these curing conditions curing degree of the plastisol is very poor and not all plasticizer has been absorbed by PVC particles; so the plasticizer (with low-molecular-weight than PVC resin) migrates easily through a microstructure characterized for its non-cohesion stage. Samples cured at 180 °C show low migration levels since the amount of free plasticizer is lower (maximum migration is about is 23% for low curing times and 1.25% migrated plasticizer is obtained for a curing time of 16 min). Migration characterization of plastisols isothermally cured at 200 °C shows the minimum values of migrated plasticizer: 0.7–0.15% range for curing times of 10 and 16 min, respectively. This is due to high cohesion state as a consequence of PVC–plasticizer interactions which prevent the plasticizer migration. For the PVC/EFAE system isothermally cured at 220 °C, the

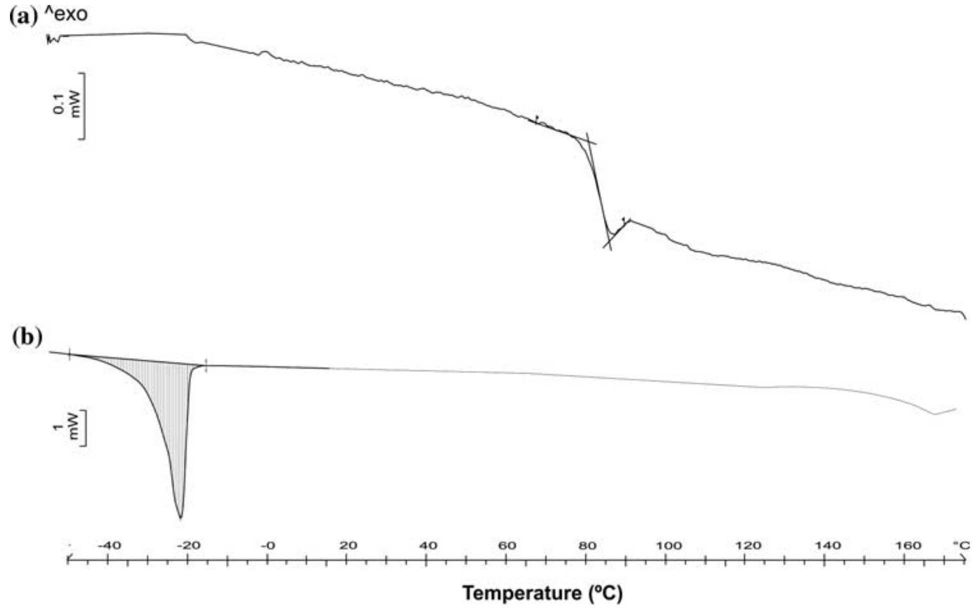

Fig. 8 DSC calorimetric curves of **a** PVC resin Lacovyl PB 1172 H-, **b** fatty epoxyester acid plasticizer 401 by Traquisa

Table 2 Results of thermal analysis obtained by DSC for plastisols with fatty acid epoxyester (EFAE) plasticizer, isothermally cured at different temperatures for different curing times

Temperature (°C)	Plastisol T_g characterization				Free plasticizer characterization			
	Time (min)	Onset (°C)	Endset (°C)	Inflection point (°C)	Normalized integral (J g^{-1})	Onset (°C)	Endset (°C)	Peak (°C)
160	8	–	–	–	−11.7	−25.1	−13.3	−17.4
	10	–	–	–	−7.2	−24.5	−13.3	−18.4
	12	−15.7	−8.8	−12.7	–	–	–	–
	14	−15.6	−8.4	−11.4	–	–	–	–
	16	−15.6	−8.5	−12.3	–	–	–	–
180	8	–	–	–	−8.0	−24.2	−13.4	−18.1
	10	−16.6	−9.6	−12.4	–	–	–	–
	12	−18.4	−9.6	−12.2	–	–	–	–
	14	−16.7	−10.7	−12.8	–	–	–	–
	16	−19.5	−10.6	−13.9	–	–	–	–
200	8	−18.8	−10.7	−13.1	–	–	–	–
	10	−19.0	−10.7	−13.3	–	–	–	–
	12	−18.5	−9.9	−12.4	–	–	–	–
	14	−17.6	−10.5	−12.5	–	–	–	–
	16	−16.2	−11.38	−12.4	–	–	–	–
220	8	−17.0	−11.5	−13.4	–	–	–	–
	10	−16.9	−12.2	−13.6	–	–	–	–
	12	−17.0	−11.7	−13.8	–	–	–	–
	14	−18.2	−10.8	−12.6	–	–	–	–
	16	−18.0	−10.2	−12.2	–	–	–	–

migration index is also low, decreasing from 2.2 to 1.5% for curing times of 6 and 10 min, respectively, but for longer times we can observed an increase in the amount of migrated plasticizer until 3.26% for 16 min of curing time due to thermal degradation.

Conclusions

The use of natural-based plasticizers derived from EFAE rises as an interesting alternative for obtaining plastisols with low toxicity. The curing process may be carried out in

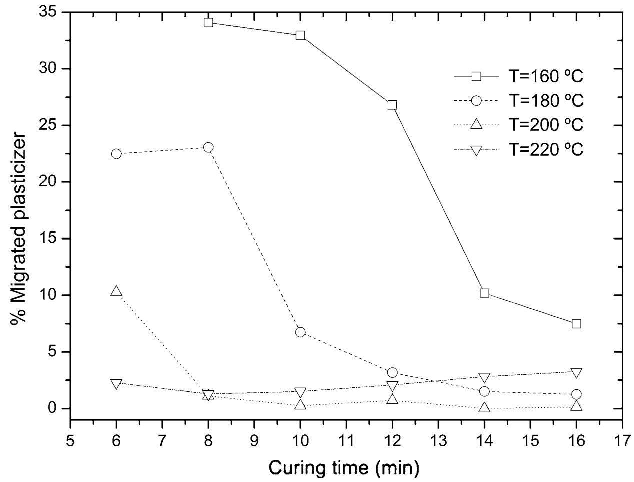

Fig. 9 Variation of percentage of migrated plasticizer for vinyl plastisols with a fatty acid epoxyester plasticizer isothermally cured at different temperatures in terms of the curing time

a suitable way at isothermal temperatures of 200 or 220 °C with curing times of about 10 and 14 min, respectively, according to the study of mechanical properties. For these curing conditions, plastisol microstructure is formed by a completely homogenous matrix due to melt of microcrystallites and the plasticizer absorption. Optimum mechanical properties are obtained for these curing conditions (tensile strength values of about 12 MPa, elongation at break close to 290%) and these are similar to PVC/DEHP and PVC/DINP systems thus showing interesting possibilities of substitution. From an industrial point of view, it is preferable the use of temperatures of 200 °C and curing times of 10 min since PVC is very sensitive to thermal degradation and long curing times lead to thermal degradation (even at lower curing temperatures).

On the other hand, from a quality control point of view, the study of the color coordinates (a^*, b^*, and L^*) is an easy method to determine the curing degree. These colorimetric parameters play an important role with the aim of defining a simple system of quality control, with low cost and fast. In addition a direct relationship between plasticizer migration as a function of temperature and curing time is detected. Regarding to this, minimum values of migration are obtained for the same curing conditions of the samples with the best mechanical properties.

Finally the calorimetric analysis allows corroborating the presence of free plasticizer not absorbed for the PVC at low temperatures and curing times.

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