

# Characterization of the Curing Process of Vinyl Plastisols with Epoxidized Linseed Oil as a Natural-Based Plasticizer

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**ABSTRACT:** In this work, we have evaluated the curing process of a natural-based plasticizer, epoxidized linseed oil, as a possible alternative to phthalate substitution for polyvinyl chloride. Several curing times ranging from 6 to 14 min at different isothermal curing temperatures in the 140–220°C range have been selected. The effects of the curing process (in terms of time and temperature) have been determined by mechanical tests, color measurements, and

microstructure characterization. The obtained results show that optimum overall properties are obtained for curing times of 10–12 min at 200°C or 8 min at 220°C, which are typical values of industrial processing of vinyl plastisols. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2550–2557, 2012

**Key words:** poly(vinyl chloride); curing of polymers; mechanical properties; additives; degradation

## INTRODUCTION

In the last 20 years, thermoplastic materials have been widely used in several industrial sectors such as food packaging, toys, electric and electronic equipment, medical devices, and so forth. It is well known that many plastic formulations contain low-molecular-weight compounds (additives) such as stabilizers, lubricants, and plasticizers. These additives are highly useful for processing purposes or to achieve certain properties (mechanical, chemical, thermal, and so forth).<sup>1,2</sup>

These low-molecular-weight additives in many cases are characterized by high mobility across the polymer structure; thus, they are capable to move from the bulk material toward the surface in a so-called migration process.<sup>3,4</sup> If the polymer (with additives in its formulation) is in direct contact with other material, it is possible to transfer a part of this additive into it and this can result in smell and/or taste changes or even some toxicological problems related to these additives ingestion.<sup>5</sup>

Flexible or plasticized polyvinyl chloride (P-PVC) is one of the most widely used polymers in several important industrial sectors such as packaging, toy, biomedicine, and building. P-PVC is characterized by the presence of high amounts of liquid plasticiz-

ers.<sup>6,7</sup> Traditionally, several phthalate-based compounds such as di(2-ethyl hexyl) phthalate (DEHP) or especially diisononyl phthalate (DINP) have been widely used as plasticizers for P-PVC formulations. At present, the use of these compounds is being questioned as a consequence of toxicity problems related to plasticizer migration.<sup>8</sup> For this reason, some countries have developed some regulations regarding the use of phthalates in P-PVC.<sup>9</sup>

For example, five phthalates have undergone European union (EU) assessments to determine whether they pose any risk to human health or the environment. The risk assessments for DINP and diisodecyl phthalate show no risks to human health or the environment for any current use. The risk assessment for DEHP shows no risk to the general population. Other countries such as the United States and Canada have developed similar regulations.

To solve or to minimize this problem, an important effort on the development of new low-toxicity and low-migration plasticizers has been studied.<sup>10–12</sup> Among the wide variety of low-toxicity plasticizers (citrate, benzoate, polymeric, and so forth), the use of epoxidized vegetable oils such as soy bean oil, castor oil, linseed oil, and fatty acid esters is an environment-friendly alternative for phthalate substitution.<sup>13–16</sup> Epoxidized natural oils are characterized by a double effect: they act as a plasticizer agent thus enhancing flexible properties and they promote a stabilization effect, as it is capable to scavenge acid groups through catalytic degradation thus having a positive effect on thermal stabilization.<sup>17–19</sup> On the other hand, they show low volatility, high resistance to solvent extraction (aqueous or hydrocarbon), and its migration tendency is almost negligible.<sup>20</sup>

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Furthermore, we have to take into account that linseed oil is a natural product, which is obtained from the seed of the common flax (binomial name: *Linum usitatissimum*) by pressure or extraction, and for its part, epoxidized linseed oil (ELO) is used as plasticizer and stabilizer in plastic materials especially for PVC and its copolymers to keep plastics and rubber soft and pliable. The epoxy functionality provides excellent heat and light stability.<sup>21</sup>

The plasticization effect is a complex process that takes part in the curing process of a liquid plastisol. A liquid plastisol is a mixture of solid PVC particles (in powder form) in a liquid matrix (plasticizer). As the liquid plastisol is heated, plasticizer enters into PVC particle voids and aggregates.<sup>22</sup> Over the PVC glass transition temperature, which is located at about 87°C, PVC individual particles aggregates absorb more plasticizer, thus promoting a solvation or swelling process.<sup>23</sup> Once the glass transition temperature has been passed, the material acquires a gel structure and the appearance is a solid paste; however, the structural cohesion is still low and subsequently mechanical response is poor. It is necessary to reach temperatures over 190°C to promote fusion of PVC microcrystallites and form, together with the absorbed plasticizer, a homogeneous structure.<sup>24,25</sup> After a cooling process, a flexible solid is obtained with mechanical performance useful for industrial use. The curing process of liquid plastisols is industrially carried out at isothermal conditions, and therefore, the main parameters governing the curing process are the isothermal temperature and the curing time.<sup>26,27</sup>

The main aim of this work is the study of the curing conditions of PVC plastisols with a plasticizer coming from natural resources as ELO. By this way, PVC plastisols were prepared with a constant plasticizer amount of 70 per hundred resin (phr), which is widely used at industrial level. The effects of temperature and time were analyzed by mechanical characterization, morphological observation, and color changes.

## EXPERIMENTAL

### Materials and procedures

A commercial PVC resin Lacovyl PB 1172 H supplied by Atofina UK (Midlands, UK) was used. The PVC was obtained by microsuspension polymerization with a *K* value of 67 (ISO 1628-2). The selected plasticizer was an ELO (CAS number 8016-11-3) with average molecular weight of 930 g mol<sup>-1</sup> supplied by Traquisa S.L. (Barcelona, Spain). This plasticizer is composed of different fatty acids in the following proportion: 4.5 wt % stearic acid, 6.5 wt % palmitic acid, 15.5 wt % linoleic acid, 19.5 wt % oleic

**TABLE I**  
Summary of the Main Characteristics of the Epoxidized Linseed Oil Plasticizer

Density at 20°C (g cm <sup>-3</sup> )	1.05 ± 0.01
Viscosity at 20°C (p)	12–16
Acid index (mg KOH g <sup>-1</sup> )	≤1
Iode index	≤5
Gardner color	≤3
Flammability point (°C)	287
Epoxide oxygen (%)	>8
Freezing temperature (°C)	–
Water solubility	Nonsoluble
Aspect at room temperature	Oilous liquid

acid, and 53 wt % linolenic acid. The main characteristics of the ELO plasticizer are summarized in Table I.

### Plastisol preparation

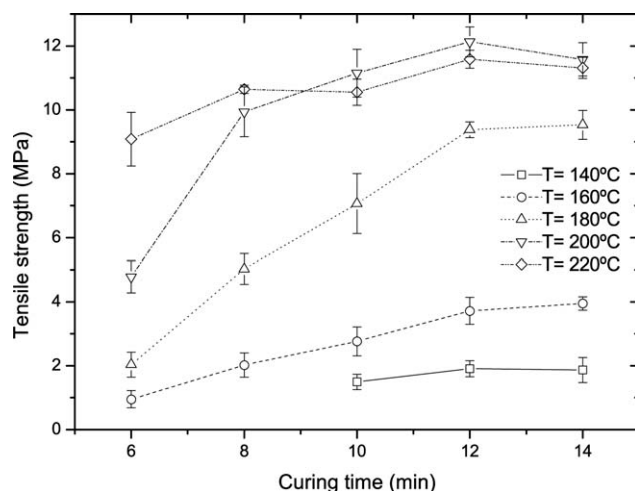
Plastisol formulation contains 70 phr of plasticizer without any additional stabilizer. The plastisols were prepared by mixing the components in a rotative mixer KAPL mod. 5KPMS (KAPL, MI, USA) for 10 min at a rotating speed of 3 rpm.

After the mixing process, the pastes were placed into vacuum chamber (HEK-GmbH, Lubeck, Germany) under reduced pressure (750 mmHg) for 15 min to reduce the volume of air bubbles entrapped in the bulk, and it was stored for 24 h and then was spread into an aluminum mold.

The curing process of the plastisol was carried out at isothermal conditions in a ventilated oven (Carbolite mod. 2416CG; Keison Products, Barcelona, Spain). The curing process was carried out at different temperatures in the 140–220°C range, and the curing time varied from 6 to 14 min. Prior to the curing process, the liquid plastisol was spread into an aluminum mold 190 × 125 mm<sup>2</sup> in size; the appropriate amount of the liquid plastisol was dosed to obtain sheets 5 mm in thickness. After a cooling process, these sheets were stamped in a die on a hydraulic press mod. MEGA KCK-15A (Melchor Gabilondo S.A., Vizcaya, Spain) to obtain standard samples for characterization tests.

### Mechanical characterization

Tensile tests were carried out using a universal tensile test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain) following the guidelines of the ISO 527. A 20 mm min<sup>-1</sup> crosshead rate was used with a load cell of 5 kN. All specimens were tested at room temperature and a minimum of five samples were analyzed, and then average values of tensile strength and elongation at break were calculated.



**Figure 1** Variation of tensile strength of PVC/ELO plastisols in terms of the curing time for different isothermal curing temperatures.

### Morphological characterization

Morphology analysis of fractured surfaces of plastisols was carried out by means of a scanning electron microscope (SEM) JEOL JSM-6300 (Jeol USA, Peabody, MA) using secondary electrons with an acceleration voltage of 15 kV. Samples were covered with a 5- to 7-nm Au layer in vacuum conditions prior to each measurement. Fractured surfaces generated from the tensile test were observed with different magnification, and a minimum of three images were analyzed for each sample.

### Color measurements

The effect of the curing conditions on surface color was determined by color coordinate measurements 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 plastisols.

## RESULTS AND DISCUSSION

### Influence of temperature and time on mechanical properties

The use of vinyl plastisols at industrial level is determined by the curing conditions in terms of the isothermal temperature and curing time; the use of the appropriate combination of temperature and time leads to optimum overall properties. If the plastisol is not fully cured, the material does not acquire enough cohesion, thus leading to early breakage. On

the other hand, when the plastisol is completely cured, the tensile strength reaches maximum values that are representative for high cohesion levels in terms of the internal structure.

Figure 1 shows a plot obtained for the tensile strength of ELO-based plastisols at different isothermal curing temperatures and different times. We can clearly observe that the use of low curing temperatures of about 140°C does not lead to good mechanical properties. The tensile strength is increased from 1.5 up to 1.9 MPa for curing times of 10 and 14 min, respectively. Lower curing times do not confer enough cohesion so the material breaks without offering any resistance. If the material is isothermally cured at 160°C, mechanical response is still poor despite tensile strength reaching up to value 3.9 MPa for curing times of about 14 min. We can observe that tensile strength increases but it remains at relatively low values, thus indicating lack of curing. The same tendency is observed for ELO-based plastisols isothermally cured at 180°C; nevertheless, as the curing temperature is higher, the tensile strength reaches the value of 9.5 MPa for curing times of 14 min. Despite this, the material remains partially cured. It is important to note that the curing process of PVC plastisols needs a threshold temperature, which depends on the PVC nature, to complete all the stages of the curing process or gelation. The use of temperatures lower than this threshold is not enough to obtain the optimum properties even for long curing times.

On the other hand, we can observe that plastisols reach high curing levels for curing temperatures of 200°C. The tensile strength changes from relatively low value of about 4.8 MPa up to value of 12.1 MPa for a curing time of 12 min. Above this curing time, we observe a very slight decrease of tensile strength (11.4 MPa for a curing time of 14 min); this is mainly related to degradation of PVC as it shows high sensitiveness to thermal degradation, and on the other hand, ELO has a higher thermal stability, and therefore, the volatilization of plasticizer is lower.<sup>28,29</sup> The degradation of PVC results in a mechanical performance loss. In addition, ELO that acts as a plasticizer has a thermal stability higher than PVC.

Similar behavior can be seen for isothermal curing temperatures of 220°C. In this case, the curing process is fast, and good high tensile strength values are obtained for curing times of 8 min (11.5 MPa). Longer curing times promote a slight increase in tensile strength up to value of 12 MPa (in the 10–12 min range). As we have described before, higher curing times (<14 min) lead to plastisol degradation and a slight decrease in tensile strength is detected.

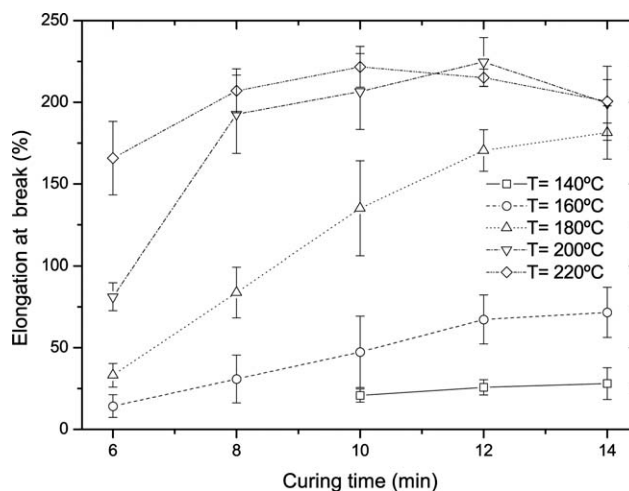
In addition to tensile strength, elongation at break shows high sensitiveness to the curing level. Figure 2 shows the plot of elongation at break in terms of

the curing time at several isothermal curing temperatures in the 140–220°C range. As plastisol acquires major cohesion, elongation at break increases in a remarkable way, thus indicating good plasticization effect.

Elongation at break follows similar tendency to that observed for tensile strength. For isothermal curing temperatures of 140°C, relatively low values of elongation at break are obtained (about 28% even for long curing times of 14 min). For the curve corresponding to elongation at break of plastisols isothermally cured at 160°C, we observe same behavior where for a curing time of 14 min, we obtain elongation at break values of about 71.6%. All these values indicate low plastisol cohesion. Plastisols isothermally cured at these conditions do not reach the appropriate particle cohesion between swollen PVC particles and plasticizer, and therefore, it is not possible to transfer stresses in an appropriate way and this fact leads to low ductile properties. Particle cohesion remarkably improves for isothermal curing temperatures of 180°C. In this case, we obtain elongation at break values of 135% and 181% for curing times of 10 and 14 min, respectively. If the curing temperature is raised to 200°C, elongation at break values are higher even for low curing times (200 and 224% for curing times of 8 and 12 min, respectively). As we have described before, PVC is very sensitive to thermal degradation and combination of high temperatures and long curing times (higher than 12 min) could lead to plastisol degradation. This fact could be responsible for the very slight decrease in elongation at break values at high curing times. If plastisols are isothermally cured at 220°C, excellent plasticization effect (high elongation at break values) was detected even for short curing times in the 8- to 10-min range. Above curing times of 10 min, a slight decrease of elongation at break is observed and this could be related to plastisol degradation as described before.

All these results highlight the complexity of the curing process. We have to take into account that a liquid plastisol is a suspension of small PVC particles and aggregates in a liquid plasticizer matrix. This system must change to a solid state through a curing process that is achieved by combination of temperature and time. As this curing process occurs, the plastisol acquires typical properties of a solid plastisol so as it has been evidenced by tensile strength and elongation at break and there is a direct relation between mechanical properties and the curing degree. As evidenced by the abovementioned results, satisfactory curing levels are obtained for a curing temperature of 200°C and curing times in the 10- to 12-min range or for a curing temperature of 220°C and a curing time of 8 min.

In general, the use of ELO as plasticizer of PVC induces a slight loss of mechanical properties com-



**Figure 2** Variation of elongation at break of PVC/ELO plastisols in terms of the curing time for different isothermal curing temperatures.

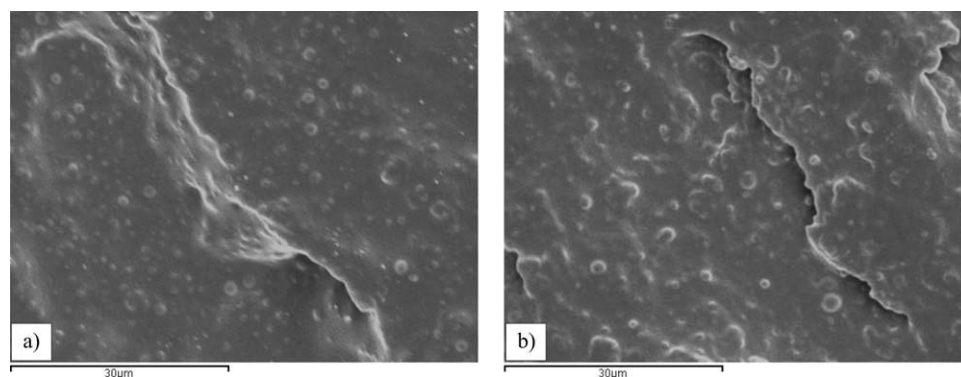
pared with traditional plasticizers; however, this reduction on mechanical performance do not prevent its use, since the resulting mechanical properties reach an acceptable value for many applications.<sup>8</sup>

#### Influence of curing parameters on plastisol structure

It is possible to study the internal structure of the PVC/ELO system by SEM analysis of fractured surfaces obtained in tensile tests. It is possible to distinguish the different stages that occur in the curing process by analyzing SEM microphotographs of fractured surfaces of plastisols cured at different conditions. In the first stage of the curing process, plasticizer starts entering into some PVC aggregates, thus leading to partial swelling. At the end of this stage, these swollen aggregates get in contact, and as a result, the microstructure will be characterized by the presence of spherical swollen aggregates with irregular profile. In Figure 3, we can observe these microstructures for plastisols isothermally cured at 160 and 200°C for 6 min. It is evident from the observation of the SEM microphotographs that the presence of spherical areas is related to swollen aggregates. At this stage, the plastisol has acquired a solid consistency but mechanical response is still too low as described before (tensile strength is about 6 MPa and the elongation at break is lower than 100%).

In the second stage, the swelling process goes on as the plasticizer enters into individual PVC particles. These two stages are directly related to PVC particle size and type of PVC, since small size and amorphous regions in PVC particles enable plasticizer entering thus enabling particle swelling.





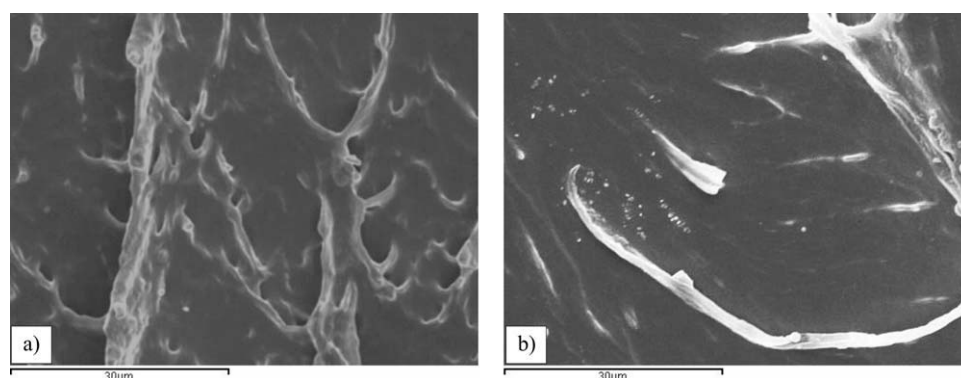
**Figure 3** SEM photomicrographs ( $\times 2000$ ) of fractured surfaces of PVC/ELO plastisols cured for 6 min at different isothermal curing temperatures: (a) 160°C and (b) 200°C.

Although plastisols show some mechanical properties at the end of these stages, it is necessary to increase temperature and curing time to produce fusion of microcrystalline domains and subsequent formation of a homogeneous structure in which these spherical formations are not detected. At this stage, the plastisol is fully cured and it shows optimum mechanical properties. Figure 4 shows SEM microphotographs of fractured surfaces of PVC/ELO plastisols isothermally cured at 200°C (curing time of 10 min) and 220°C (curing time of 8 min). We observe a homogeneous structure that is representative for PVC microcrystallites fusion. Plastisols cured at these conditions show good mechanical response due to the high cohesion reached after particle swelling and fusion of crystallites. Tensile strength values are close to 10 MPa and elongation at break is around 200%. These are interesting properties but it is necessary to complete the curing process by using higher curing times or higher temperatures to get the optimal mechanical properties. We can observe the surface morphology in Figure 4. As PVC plastisols are highly ductile, we can see evidence of plastic deformation on these SEM microphotographs: rounded crests and valleys since the material flows due to good plasticizing effect; this fact leads to the

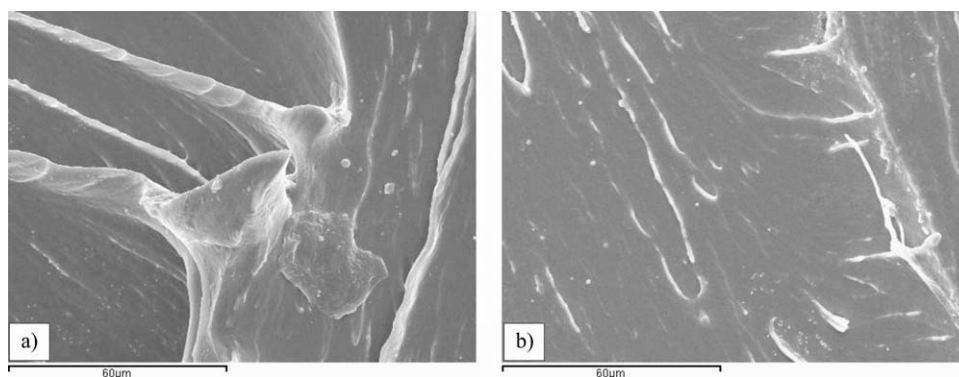
formation of high-profile caves typical of a ductile fracture. On the other hand, this homogeneous structure is responsible for good tensile strength values.

Figure 5 shows SEM microphotographs of fractured surface of fully and partially degraded PVC/ELO plastisols (isothermal curing temperature of 200 and 220°C and curing time of 14 min). We observe a homogeneous and smooth structure in which some pronounced crests/waves are detected. We do not see evidence of rounded caverns as described before, which are representative for ductile deformation. So, we can establish a relationship between the homogeneous and smooth structure and mechanical performance of plasticized PVC. The long curing time (14 min) has produced some plastisol degradation that leads to a slight embrittlement. Some microcracks appear and after a plastic deformation, these cracks form the typical wave structure. As we have observed before, the mechanical response of the plastisol at these conditions is still good, but a slight decrease in tensile strength and elongation at break is detected.

Figure 6 shows in a clear way (high magnification) the change in plastisol structure in terms of the isothermal curing temperature at a curing time of 6 min. For low curing temperatures of 160°C, we



**Figure 4** SEM photomicrographs ( $\times 2000$ ) of fractured surfaces of PVC/ELO plastisols cured at different isothermal temperatures ( $T$ ) and curing times ( $t$ ): (a)  $T = 200^\circ\text{C}$ ;  $t = 10$  min and (b)  $T = 220^\circ\text{C}$ ;  $t = 8$  min.



**Figure 5** SEM photomicrographs ( $\times 1000$ ) of fractured surfaces of PVC/ELO plastisols cured at different isothermal temperatures ( $T$ ) for a curing time ( $t$ ) of 14 min: (a)  $T = 200^\circ\text{C}$  and (b)  $T = 220^\circ\text{C}$ .

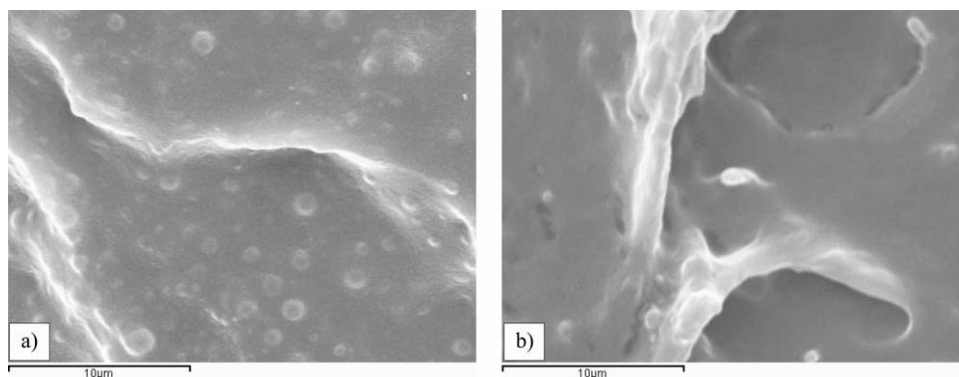
observe a heterogeneous surface characterized by the presence of spherical areas attributable to swollen PVC particles and aggregates, and this is responsible for the poor mechanical response. On the other hand, if the curing process is carried out at  $220^\circ\text{C}$ , the different stages described before are adequately completed and then we obtain a homogenous, smooth, and uniform matrix, which is typical of a fully cured plastisol. Furthermore, we see evidence of plastic deformation (rounded caverns).

#### Influence of temperature and time on degradation

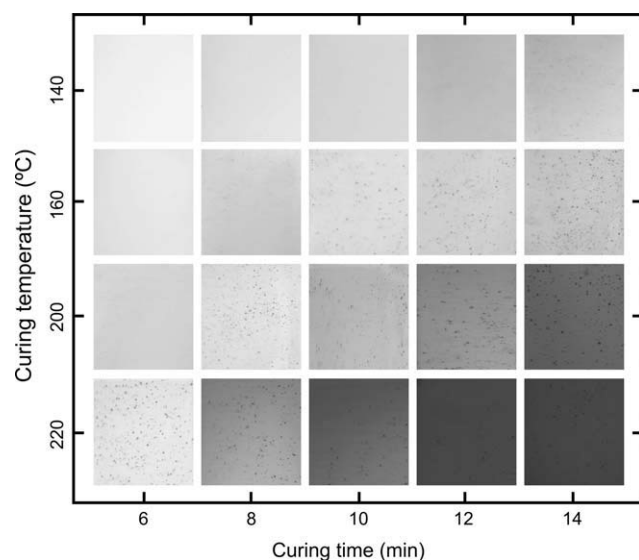
As described before, the use of SEM techniques on fractured surfaces is useful to characterize the curing process. In addition to the use of these techniques, the effects of the curing process can also be followed by simple observation of color acquired after the curing process. In general terms, color of plastisols based on ELO is slight yellow since this plasticizer shows this color at room temperature. Colorimetric techniques are very useful to define temperature and time ranges in which optimum cured plastisols are obtained. These methods are based on measurement of colorimetric coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ) as well as other parameters as yellowness index and color

change. It is possible to establish a relation between surface color of cured plastisols and overall performance. If the plastisol shows a very low curing degree, it shows whiteness and opaque color; as the curing process begins, this color changes to slightly yellow and transparency increases until plastisol is fully cured. At this stage, plastisol will show a slight yellow color and total transparency which is representative for total plasticizer absorption and formation of a homogenous matrix. Degraded plastisol (combination of high curing temperature and long curing time) will show a brownish/orange color and still will show high transparency.

Figure 7 shows a matrix representation of the color changes of plastisols in terms of the curing conditions. Samples isothermally cured at  $160^\circ\text{C}$  do not reach enough curing degree even for long curing times. As we can see in Figure 7, a white color is detectable for all curing times. Regarding plastisols isothermally cured at  $180^\circ\text{C}$ , our previous results showed interesting mechanical properties only for long curing times (always lower than fully cured plastisols) and in that case we can observe a slight yellow color for samples isothermally cured at  $180^\circ\text{C}$  and curing times in the 12- to 14-min range. Samples cured at 200 and  $220^\circ\text{C}$  and curing times of 10 and 8



**Figure 6** SEM photomicrographs ( $\times 5000$ ) of fractured surfaces of PVC/ELO plastisols cured at different isothermal temperatures ( $T$ ) and curing times ( $t$ ) of 6 min: (a)  $T = 160^\circ\text{C}$  and (b)  $T = 220^\circ\text{C}$ .



**Figure 7** Matrix representation of PVC/ELO color for different curing conditions in terms of the isothermal curing temperature ( $T$ ) and curing time ( $t$ ).

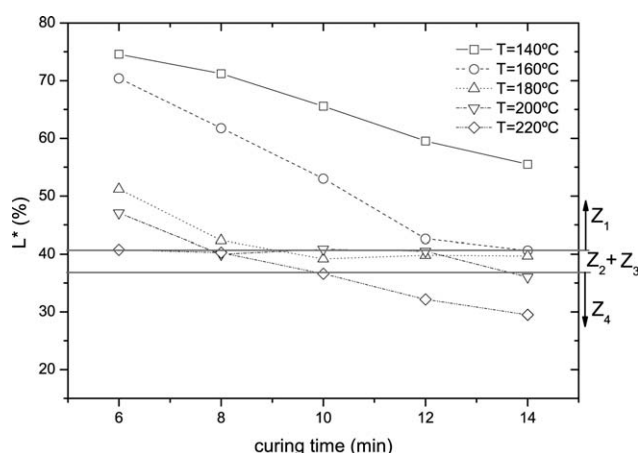
min, respectively, offer optimum mechanical response as observed by mechanical characterization. Furthermore, the SEM study has revealed a homogeneous structure. In Figure 7, we can see in a clear way that plastisols cured at these conditions show a yellowness color which is representative for fully curing. As it can be observed in Figure 7, longer exposure times for these isothermal curing temperatures lead to orange/brownish color, thus indicating that some thermal degradation has occurred.

Color variations discussed above is useful from a qualitative point of view; nevertheless, to use color information for quality control, it is useful to quantify color coordinates. Figure 8 shows the lightness ( $L^*$ ;  $L^* = 0$  indicates black and  $L^* = 100$  indicates white) in terms of the curing time for several isothermal curing temperatures in the 140–220°C. It is possible to define the variability range for lightness to ensure optimum curing conditions together with the results obtained before. We can see that plastisols isothermally cured at 140°C lightness varies from 74% to 55% for curing times of 6 and 14 min, respectively. Regarding plastisols cured at 160°C, lightness changes from 70% up to 40% for curing times of 6 and 14 min, respectively. As we have described before, these plastisols are poorly cured; so, high lightness values are related to poor curing conditions. Plastisols isothermally cured at 180°C show a lightness change from 51% to 39% for curing times of 6 and 10 min, respectively, and lightness remains almost constant with longer curing times. In a similar way, the PVC/ELO system cured at 200°C acquires yellow color for a curing time of 8 min with a luminance value of 40%, which remains almost constant; at longer curing times (14 min),

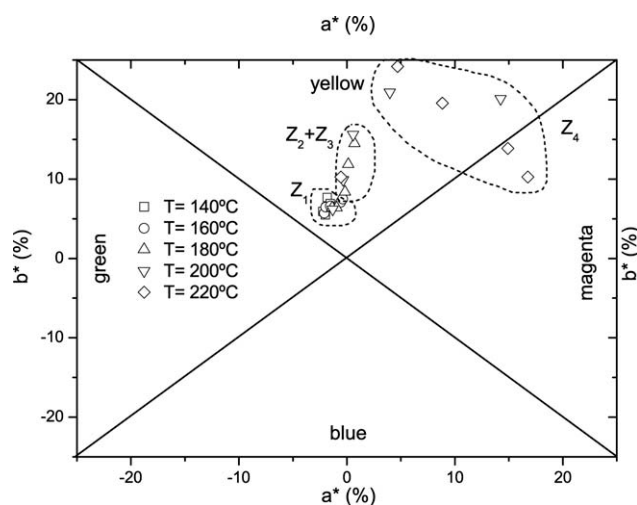
luminance reaches a value of 36% and these plastisols seem to be slightly degraded. For plastisols isothermally cured at 220°C, luminance changes from 40% to 29% for curing times of 6 and 14 min, respectively.

Taking into account the abovementioned luminance results, it is possible to establish two luminance threshold values. Luminance values lower than 36% (Zone  $Z_4$ ) are representative for fully cured and degraded plastisols (orange and brownish color). On other hand, luminance values higher than 40% (Zone  $Z_1$ ) indicate poor curing degree (whiteness color). The zone comprised between  $Z_1$  and  $Z_2$  contains partially cured ( $Z_2$ ) and fully cured ( $Z_3$ ) plastisols, but it is difficult to separate them since luminance values change in a narrow range and are overlapped. Nevertheless, a deep analysis of  $a^*$  and  $b^*$  color coordinates allows to identify these two zones. It is important to remark that  $a^* > 0$  tends to red and  $a^* < 0$  tends to green while  $b^* > 0$  tends to yellow and  $b^* < 0$  tends to blue. Hence, the evolution of these color coordinates can be useful to know the degree of curing of a plastisol together with the luminance study.

Figure 9 shows  $a^*$  and  $b^*$  color coordinates in a four-quadrant (red, green, yellow, and blue) graph. Poorly cured plastisols (Zone  $Z_1$ ) show low  $a^*$  and  $b^*$  values; as the curing degree increases the yellowish color is more intense and we can observe a zone  $Z_2 + Z_3$  representative for high curing degree plastisols. If plastisols are fully cured, intense yellowish color is detected so that an important increase in  $b^*$  is representative of these curing conditions while  $a^*$  coordinate remains almost constant. On other hand, if plastisols are degraded (combination of high temperatures and long curing times), we observe an intense orange/brownish color, then the  $a^*$  and  $b^*$  coordinates increase in a remarkable way (Zone  $Z_4$ ). So, it



**Figure 8** Variation of luminance ( $L^*$ ) of PVC/ELO plastisols in terms of the curing time for different isothermal curing temperatures.



**Figure 9** Representation of color coordinates ( $a^*$ ,  $b^*$ ) of PVC/ELO plastisols for different isothermal curing temperatures ( $T$ ) and curing times ( $t$ );  $Z_1$ : low curing temperatures;  $Z_2$ : medium curing temperatures;  $Z_4$ : high curing temperatures.

is possible to know the degree of curing of a plastisol by a simple colorimetric study of luminance ( $L^*$ ),  $a^*$ , and  $b^*$  coordinates.

### CONCLUSIONS

Plastisols cured at 200°C with curing times in the 10- to 12-min range or at 220°C with lower curing times (8 min) exhibited the best set of mechanical properties. The use of these curing conditions leads to optimum mechanical response of plastisols with tensile strength values of about 12 MPa and elongation at break around 250%. The optimum mechanical response is directly related to plastisol microstructure during different stages in the curing process. A SEM study has revealed that significant changes in microstructure can be detected for poorly cured, fully cured, and degraded plastisols.

On other hand, from an industrial point of view, it is possible to define a simple method to determine the degree of curing of a plastisol. This method is based on a colorimetric study by determining color coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ) that allows identifying different zones corresponding to poorly cured, almost cured, fully cured, and degrade plastisols, and this

is an interesting tool for quality control at industrial scale.

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### References

- Braun, D. J. *Vinyl Addit Technol* 2001, 7, 168.
- Jimenez, A.; Lopez, J.; Iannoni, A.; Kenny, J. M. *J Appl Polym Sci* 2001, 81, 1881.
- Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. *Polym Test* 2008, 27, 221.
- Wang, Q.; Storm, B. K. *Polym Test* 2005, 24, 290.
- Pedersen, G. A.; Jensen, L. K.; Fankhauser, A.; Biedermann, S.; Petersen, J. H.; Fabech, B. *Food Addit Contam* 2008, 25, 503.
- Kim, S. W.; Kim, J. G.; Choi, J. I.; Jeon, I. R.; Seo, K. H. *J Appl Polym Sci* 2005, 96, 1347.
- Wang, G. Q.; Chen, Y. T. *Polym Test* 1991, 10, 315.
- Crespo, J. E.; Balart, R.; Sanchez, L.; Lopez, J. *J Appl Polym Sci* 2007, 104, 1215.
- Shea, K. M. *Pediatrics* 2003, 111, 1467.
- Audic, J. L.; Reyx, D.; Brosse, J. C. *J Appl Polym Sci* 2003, 89, 1291.
- Fankhauser-Noti, A.; Grob, K. *Trends Food Sci Tech* 2006, 17, 105.
- Hakkarainen, M. *Adv Polym Sci* 2008, 211, 159.
- Abdelbary, E. M.; Badran, B. M.; Khalifa, W. M.; Yehia, A. A. *Elastomerics* 1978, 110, 38.
- Benaniba, M. T.; Belhaneche-Bensemra, N.; Gelbard, G. *Polym Degrad Stab* 2001, 74, 501.
- Kanno, S.; Kawamura, Y.; Mutsuga, M.; Tanamoto, K. *J Food Hyg Soc Jpn* 2006, 47, 89.
- Kawamura, Y.; Kanno, S.; Mutsuga, M.; Tanamoto, K. *J Food Hyg Soc Jpn* 2006, 47, 243.
- Lee, J. H.; Park, C. W.; Noh, I. *Polymer (Korea)* 1995, 19, 543.
- Starnes, W. H.; Du, B.; Kim, S.; Zaikov, V. G.; Ge, X. L.; Culyba, E. K. *Thermochim Acta* 2006, 442, 78.
- Taghizadeh, M. T.; Nalbandi, N.; Bahadori, A. *Express Polym Lett* 2008, 2, 65.
- Fenollar, O.; Garcia-Sanoguera, D.; Sanchez-Nacher, L.; Lopez, J.; Balart, R. *J Mater Sci* 2010, 45, 4406.
- Ozturk, C.; Kusefoglul, S. H. *J Appl Polym Sci* 2010, 116, 355.
- Boudhani, H.; Laine, C.; Fulchiron, R.; Cassagnau, P. *Rheol Acta* 2007, 46, 825.
- Fenollar, O.; Garcia, D.; Sánchez, L.; López, J.; Balart, R. *Eur Polym J* 2009, 45, 2674.
- Garcia, J. C.; Marcilla, A. *Polymer* 1998, 39, 3507.
- Marcilla, A.; Garcia, J. C. *Eur Polym J* 1998, 34, 1341.
- Kwak, S. Y. *Polym Eng Sci* 1995, 35, 1106.
- Fenollar, O.; Sanchez-Nacher, L.; Garcia-Sanoguera, D.; López, J.; Balart, R. *J Mater Sci* 2009, 44, 3702.
- Sharma, V.; Kundu, P. P. *Prog Polym Sci* 2006, 31, 983.
- Sharma, V.; Kundu, P. P. *Prog Polym Sci* 2008, 33, 1199.