Formulation and Mechanical Characterization of PVC Plastisols Based on Low-Toxicity Additives

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ABSTRACT: New formulations of plastisols based on low-toxicity plasticizers were proposed and characterized. Traditional phthalate plasticizers were replaced in the plastisols studied in this research by polymeric plasticizers (i.e., saturated polyesters), produced by the reaction of a diol and a carboxylic acid. The main drawback for the use of these plasticizers in formulations of PVC plastisols is a significant increase of the paste viscosity, which decreases their processability; thus, the use of additional additives to reduce viscosity is recommended. This study also includes the optimization of the processing conditions (cure temperature and time) of the proposed plastisols: complete cure was obtained at 140°C and 10 min. It is reported that the final properties of plastisols are very sensitive with respect to the processing conditions; in fact, insufficient plasticization or degradation can affect the material when processed out of the optimum conditions. The influence of the plasticizer concentration on mechanical and optical properties, such as tensile strength, hardness, brightness, and the like, is also reported. In summary, the proposed plastisols, with low-toxicity plasticizers, offer a valid alternative to traditional PVC plastisols based on phthalate plasticizers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1881–1890, 2001

Key words: plastisols; PVC; plasticizer; mechanical properties; viscosity; cure

INTRODUCTION

PVC compounds are multicomponent systems formed by a PVC resin and some additives, that is, plasticizers, stabilizers, or fillers. Among the additives, plasticizers are the most frequently used because they are necessary for industrial processing to improve some PVC properties like flexibility and workability. Dialkyl phthalates are widely used as plasticizers because they exhibit high compatibility with PVC as well as low cost and good properties for industrial processing.[1] Low molecular weight phthalates offer high efficiency and mixing ability, although they are too volatile and their migration and diffusion into the plastisol are too high. Other phthalates, such as diisononyl phthalate (DINP) and diethylhexyl phthalate (DEHP), are more frequently used because of their lower volatility.

However, despite the excellent properties provided to plastisols, the use of phthalates is being questioned because of their potential toxicity to humans and the environment and their high migration into the plastisol structure.[2–5] On the other hand, high molecular weight compounds (with lower volatility) may be used as alternative plasticizers in PVC formulations. In fact, some polymeric molecules have been proposed as potential alternatives to phthalates,[6] but they have not been used extensively in plastisol formulations. Most of these candidates are saturated polyesters obtained from the reaction between a diol and a carboxylic acid, and their properties vary according to the reagents and their condensation grade. Normally, an alcohol or a monocarboxylic acid is added to the original formulation to stop further polymerization. The basic difference with monomeric plasticizers is their high molecular weight, which probably indicates low diffusion into the plastisol; however, some low molecular weight fragments may be liberated at high temperatures.[7–9] Moreover, they also present some drawbacks when compared to phthalates, such as high viscosity and lower plasticization efficiency. These important disadvantages may be overcome using an additional reagent with lubricant properties. Obviously, the additional compounds must also be nontoxic products.

Another possible solution to the problem of the high viscosity of the plastisols obtained in this way could be an increase of processing temperature. However, this solution raises another problem, which is the possibility of working at temperatures closer to those at which the thermal degradation starts. As is well known, PVC-based materials present a limitation: they are all subject to degradation. This limited resistance to degradation may cause a clear decrease in mechanical properties, so a careful study of cure conditions (mainly temperature and time) is required.

Degradation of PVC during processing and use has been the subject of numerous investigations in recent years.[1,10–18] Most of them are devoted to the study of dehydrochlorination of the pure polymer in an inert atmosphere, although PVC is most often used in plasticized form, with the amount of plasticizer being as high as 50%. This makes the problem of PVC thermal degradation very complex and requires consideration of all processes such as polymer crosslinking and plasticizer diffusion in the plastisol. To avoid such processes, a strict control of cure conditions is absolutely necessary.

The use of thermal stabilizers or flame-retardant additives may be a solution to this problem and many new formulations are currently being proposed.[19,20] However, most of the formulations are based on the use of some compounds that are able to migrate and are potentially toxic. Because one of the main goals of the present work is the proposal of nontoxic formulations, the use of such additives has to be highly controlled.

Once the formulations have been cured, their mechanical characterization is necessary to know ifwhether the properties of the final product would be good enough to permit the use of these new products compared to properties of the usual PVC–DEHP or PVC–DINP formulations. The main mechanical properties, such as tensile strength, modulus, elongation, and hardness, must be studied to get a complete characterization.

In addition, a study of the color of the plastisols must be performed as an indication of the grade of thermal degradation of the sample, especially when high temperatures and/or times of cure need to be used. The coloration of PVC formulations (the chromophore effect) is a consequence of the polymer dehydrochlorination, because it is apparent at very early stages of reaction, after elimination of as little as 0.1 to 0.2 wt % of HCl, before the consequences of decreased chlorine content or crosslinking can be detected. The use of a method to measure brightness in PVC derivatives was previously suggested[21] and some correlations may be carried out.

No previous studies of these new plastisols have been reported, so the aim of this study is the optimization of the formulation of plastisols based on low-migration additives and their complete characterization to verify their processability and service properties.

EXPERIMENTAL

Materials

Vestolit 7021 (HULS, Germany) was used as PVC raw material. This is a suspension-produced polymer non-prestabilized and capable of forming low-viscosity pastes. This resin, normally used in rotational molding, was characterized by determining some properties mainly related to the mo-

Table I   Chemical Properties of the Different Plasticizers Used in the Present Work

PVC (100) + Plast (60)	Percentage Extraction	Migration (mg) (1 cm², 6 h)
Adilene-150	14.9	0.001
DEHP	44.9	0.012
DINP	89.9	0.015

lecular weight. The molecular weight obtained by means of gel permeation chromatography (Shimadzu LC-10AD; Shimadzu, Japan) was 1.35 $\times 10^5$. A K value of 72.0, related to the viscosity of the resin and plasticizer mixture, was obtained by application of the DIN 53-726 standard.

Propyleneglicol adipate (Adilene, Traguisa, Spain) was used in the present work as a polymeric plasticizer for PVC formulations. Because there are some different commercial combinations of Adilene, some previous viscosity tests were performed on the PVC pastes obtained, and because the plasticizer Adilene-150 had a lower viscosity, it was selected for the preparation of the plastisols. Furthermore, extraction and chromatographic tests (Shimadzu GC-17A) were carried out to compare its migration behavior with that of DEHP and DINP. Results of percentage extracted and migration for pastes cured at 150°C and 10 min are presented in Table I. It can be observed that the amount of plasticizer extracted, as well as migrated, is clearly lower for Adilene-150 than that for the traditional plasticizers DEHP and DINP.

To limit the thermal degradation of the formulations obtained, a previously characterized thermal stabilizer, Irganox 1076 (Ciba-Geigy, Switzerland),[16] was added to the plastisols in an amount of 2.0 parts per hundred resin (phr). In some of the plastisols 6 wt % of an industrial lubricant (Edenol, Traguisa, Spain) was added to reduce the viscosity of pastes.

Plastisols were prepared by mixing adequate amounts of resin and plasticizer in a Brabender P-600 mixer over a period of 20 min and 23 ± 2°C. This instrument was built according to the DIN-54-802 German Standard. The paste obtained was then put in a vacuum dryer for 5 min. Once air was eliminated from the pastes, they were ready for cure according to the selected conditions for every plastisol. Samples for mechanical characterization were cut with an adequate tool to get the final standard form.

Equipment

A Brookfield viscometer B.V.II (Brookfield Instruments, USA) was used to determine the viscosity of the different plastisols according to the procedure described by the Spanish standard UNE-53-307-77. Variations in tensile strength, modulus, and elongation were followed using an Instron 6000 machine with two different rates, 1 and 50 mm/min. The former was used to determine modulus, whereas the latter was used to determine the tensile strength on 4 × 8-mm samples specially prepared for the test. Shore A–hardness measurements were carried out by the use of a Bareiss Exeta HP-DRS, according to the standard UNE-53-130, with the use of 3-mm-thick samples. Finally, color studies were performed with a Chroma-Meter CR-200 (Minolta, Tokyo, Japan) with an 8-mm measurement area, representing three different parameters: a* (red grade), b* (yellow grade), and L* (brightness), according to the UNE-53-387-86 standard.

Measurements of extraction and migration of plasticizers were carried out by a preliminary supercritical fluid extraction (ISCO-220; ISCO, Lincoln, NE) and further determination by gas chromatography. Extractions were carried out with supercritical CO_2 at 95°C and 5000 psi with 2 min of stabilization of samples in the flow of the supercritical fluid and a further 2-min extraction time. Migration was measured by extraction in physiological conditions (saliva simulant at 37°C) for 2 h and further measurement by gas chromatography.

RESULTS AND DISCUSSION

Some general properties of the prepared plastisols were determined to assess their application in industrial formulations. The selected properties to be determined were viscosity; mechanical properties, such as tensile strength, modulus, elongation (%), and hardness; and, finally, optical properties.

Viscosity

The viscosity of the different plastisols as a function of the plasticizer amount is shown in Figure 1. Two sets of results are presented, one of which is referred to the formulations with no addition of a lubricant and the other with 6% of lubricant. It
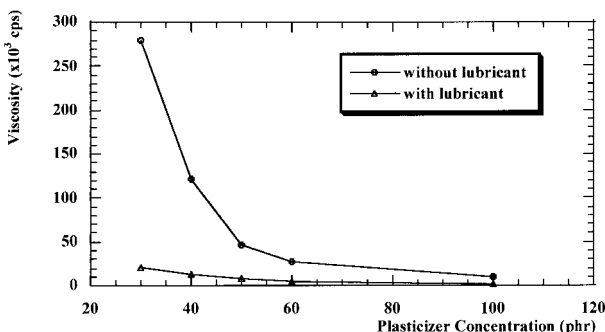
Figure 1   Viscosity of pastes prepared with different concentrations of Adilene-150.

Table II   Interaction Parameter (ν_e) for Various PVC–Plasticizer–Lubricant Mixtures

Adilene Concentration (phr)	ν_e	
	With Lubricant	Without Lubricant
30	0.07	0.03
40	0.11	0.08
50	0.12	0.09
60	0.25	0.12
100	0.58	0.21

can be observed that there is a general decrease in viscosity of pastes when the plasticizer concentration is increased. If the concentration of the plasticizer is greater than 60 phr, the plastisol presents a viscosity similar to that of the pure plasticizer. It must also be noted that general results for the nonlubrified pastes are clearly higher than those obtained for the PVC–DEHP formulations, thus making their use as adequate plastisols for industrial processing more difficult. Therefore, the addition of a lubricant is absolutely necessary to avoid such a problem. Viscosities obtained for lubricated pastes are lower than those for nonlubricated formulations at least by one order of magnitude and are similar to those of industrial plastisols.

There is no general theory to explain the behavior of the mixtures of a polymer with two low molecular weight liquids, such as plasticizer and lubricant, which results in an important decrease of viscosity. As can be observed in Figure 1, the relationship between viscosity and concentration of plasticizer is not linear and both curves seem to fit a similar equation. The viscosity could be determined taking into account the following general equation[6]:

$$\ln \nu = \sum x_i \ln \nu_i + \ln \nu_e \qquad (1)$$

where ν is the viscosity of the mixture; x_i is the concentration of the compound i and ν_i its viscosity; and the factor ν_e is the parameter representing the interaction between the components of the mixture. In this particular case, the ν_e parameter can be calculated for different concentrations of the plasticizer in the plastisol, the results of which are presented in Table II. As can be observed, higher plasticizer concentrations are

characterized by higher ν_e values, indicating a high interaction between both compounds. The results of the interaction parameter of nonlubricated plastisols are clearly lower than those of formulations in which a lubricant is used. Therefore, it can be concluded that the use of lubricants is necessary to prepare plastisols with adequate viscosity for industrial processing.

Mechanical Properties

The mechanical properties were measured for plastisols with different plasticizer concentrations cured at 155°C and 10 min. The variation in tensile strength with the concentration of plasticizer is shown in Figure 2. It can be observed that an increase in plasticizer concentration has the effect of a general nonlinear decrease in tensile strength for all plastisols, either with or without lubricant, thus rendering plastisols more flexible. The nonlinear behavior is mainly reflected in the region between 40 and 60 phr, in which the results obtained are almost constant. These results suggest that plastisols with plasticizer concentra-
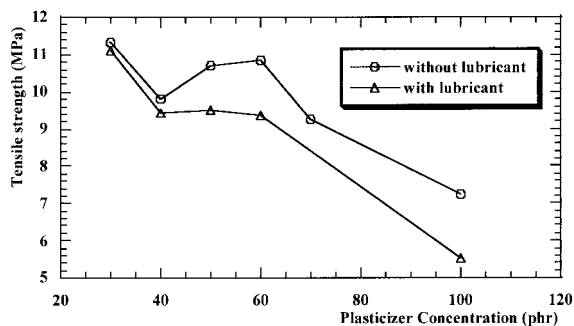

Figure 2   Tensile strength of plastisols with different concentrations of Adilene-150 (cured at 155°C, 10 min).
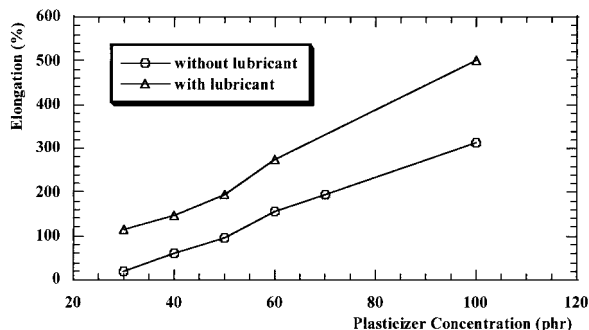
Figure 3 Elongation of plastisols with different concentrations of Adilene-150 (cured at 155°C, 10 min).

Figure 4 Modulus of plastisols with different concentrations of Adilene-150 (cured at 155°C, 10 min).

tion higher than 40 phr are characterized by a complete miscibility between the PVC resin and the plasticizer. High tensile strength values at concentrations lower than 40 phr can be explained by considering that the plasticizer concentration is too low to get a perfect blending with the PVC. On the other hand, at concentrations higher than 60 phr, an excess of plasticizer is present and the tensile strength drops. It can be also noted that PVC pastes with lubricant exhibit lower tensile strength (approximately 15% less) than that of pastes without any other additive, regardless of plasticizer. However, this result can be considered acceptable when it is compared against that of PVC–DEHP mixtures[6] and considering the advantages in processability of using a lubricant.

The variation of the elongation at break with the plasticizer concentration is shown in Figure 3. As expected, a continuous increase of the elongation with the plasticizer concentration is observed. In fact, the addition of increasing amounts of plasticizer leads to the insertion of some polar bonds between PVC macromolecular chains, with the final result of a clear increase in the elongation of plastisols. Following the tensile strength results, the presence of lubricant reduces the elongation at break of the plastisol formulations.

The elastic modulus of the materials studied was also measured and the results obtained are reported in Figure 4. The form of the curves is similar to that shown by tensile strength results as a function of the plasticizer concentration (Fig. 2). Not only do plastisols with a low plasticizer concentration exhibit a relatively high modulus and a rigid structure, with a notable decrease when this concentration is raised, but they also exhibit a behavior similar to that of elastomers.

A clear decrease of hardness–Shore A with the plasticizer concentration is shown in Figure 5.
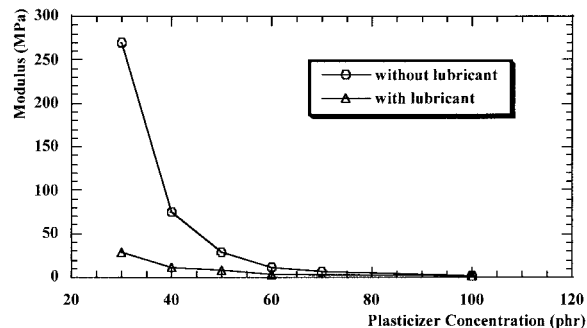
The addition of increasing amounts of plasticizer interacting with the PVC chains reduces the density of covalent bonds in the polymeric system, giving rise to a network with many polar forces and causing the observed decrease in hardness and other mechanical properties, as previously indicated. In addition, a significant reduction of the mechanical behavior can be observed for lubricated plastisols.

The conclusion of this segment of the study is the selection of the best formulation to carry out a further study of the optimization of the cure conditions. It has been proved that the plastisol with 60 phr of Adilene is the best selection because it exhibits viscosity results as well as mechanical properties similar to those obtained for industrial PVC–DEHP formulations (see Table III).

Cure of Plastisols: Temperature Effects

The cure of plastisols is characterized by two main problems. It is necessary to select temperature and time conditions high enough to get a
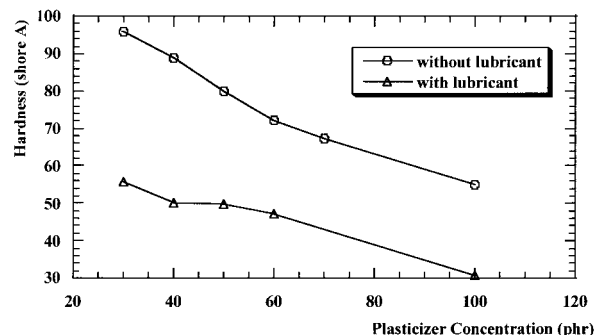

Figure 5 Hardness of plastisols with different concentrations of Adilene-150 (cured at 155°C, 10 min).

Table III   Comparison of Properties of Polypropylene–Glicol Adipate–and DEHP-Based PVC Plastisols

Formulation	η ($\times 10^3$ cps)	σ_{ut} (MPa)	ε_{ut} (%)	E (MPa)	Hardness (Shore A)
PVC : Adilene (100 : 60)	9.7	9.4	155	6.2	49.0
PVC–DEHP (100 : 70)	3.7	5.7	166	5.0	67.6

correct gelation and/or fusion of the plastisol, but not too high to avoid the beginning of thermal degradation. Therefore, a complete study of temperature and time of cure is necessary to optimize such conditions and to permit the complete characterization of the plastisols. This study was performed with a plastisol with 60 phr of plasticizer. The optimization of the cure temperature was carried out by the preparation of a paste with the selected formulation and cure in an oven for 10 min at the temperature selected between 110 and 170°C in intervals of 10°C. Mechanical properties (tensile strength, elongation, modulus, and hardness) as well as optical properties (brightness) were measured as a function of the cure temperature. In addition, and as an important parameter in the study, an investigation of the extraction and migration of such plastisols was also carried out, to be sure that there was no significant migration of plasticizer under cure conditions.

Figure 6 shows the variation of tensile strength with the cure temperature. It can be observed that an increase in temperature results in an increase in tensile strength. This can be explained, if considering that a minimum temperature is necessary to get a complete gelation of the paste. If temperatures are not high enough, the mixture between the PVC resin and the plasti-

cizer is not complete and the degree of diffusion of plasticizer molecules into the PVC macromolecular structure is too significant. It can be also observed that the increase in tensile strength is not linear and three different regions can be identified. First of all, a slight increase is observed between 110 and 140°C, which corresponds to the region in which the gelation process is predominant over any other reaction. At low temperatures (110–130°C) the movement of plasticizer molecules is too high and the cure is not complete. In the middle region (150–160°C) the system shows a saturation effect, with only a slight increase of the tensile strength. At higher temperatures degradation probably starts. At 155°C the gelation process has been completed and the thermal degradation has not yet started. A similar behavior is exhibited for the elongation results, as can be observed in Figure 7. The variation of modulus for the different cure temperatures is shown in Figure 8. The explanation of the different regions in the curve is similar to that of tensile strength, with the three regions indicated earlier. The same behavior can be observed for hardness, as shown in Figure 9.

As previously indicated, a study of the color of samples is important to determine the starting point of thermal degradation. In fact, values of HCl release as low as 0.1% are enough to signif-
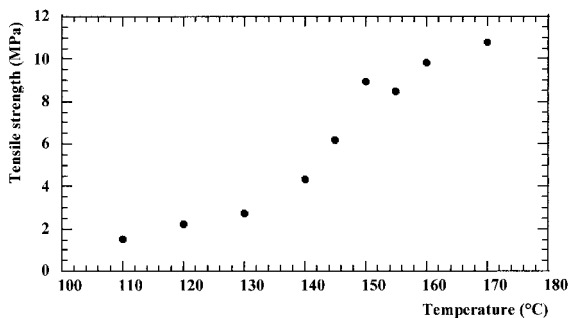

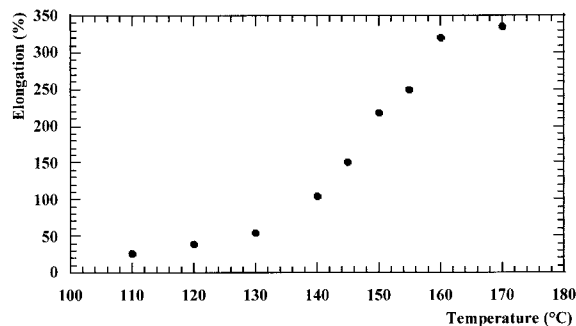**Figure 6** Tensile strength of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

Figure 7 Elongation of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).
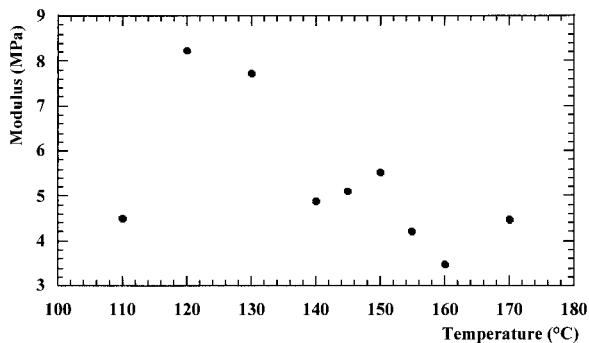
Figure 8 Modulus of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

Figure 10 Brightness of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

icantly change the color of the plastisol. This color may be measured by means of a three-parameter analysis, two of which are based on the color grade (red and yellow) and the third is based on the measurement of brightness. Color of the cured pastes was measured and no significant changes in color grade were observed, although some significant changes in brightness were measured, as shown in Figure 10. There are no changes in brightness for temperatures lower than 140°C, which means that no degradation is present as such low temperatures. From 140 to 170°C, however, a clear decrease in brightness is observed and the plastisol exhibits a slightly dark color, the change of which is more significant for the highest temperature. It is clear that some thermal degradation is initiated at temperatures as low as 150°C, which is lower than that of the degradation reaction observed for industrial PVC–DEHP plastisols. This behavior can be confirmed by the thermal characterization of these samples compared with that of the usual plastisols.[18] To conclude this segment of the study, it can be estab-
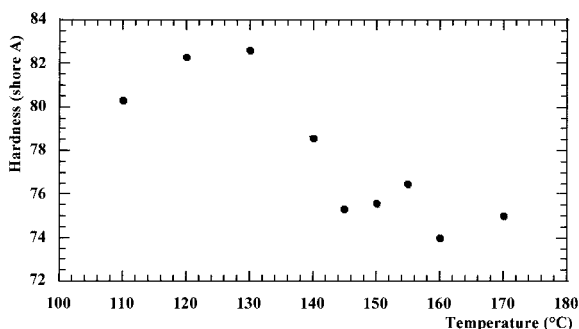
lished that 140–150°C is a good temperature range for the cure of plastisols formulated with PVC and Adilene because good mechanical properties are observed, the gelation process is completed, and the thermal degradation reaction has not yet started.

An additional but important point in this part of the study is the analysis of the extraction and migration of plasticizers for these plastisols cured at different temperatures. The main goal should be the determination of the cure temperatures, to obtain a paste with a higher resistance to diffusion and extraction of additives. Extraction results are presented in Figure 11 as a function of the cure temperature. As can be observed, the amount of plasticizer extracted from a plastisol sample clearly shows a minimum in the region of cure temperatures between 140 and 160°C. This behavior can be explained in terms of the different stages of the plasticization and cure process. Thus, the high results obtained at 110°C are explained for the consideration of the incomplete gelation. Most of the molecules of plasticizer are therefore not linked to the macromolecular struc-
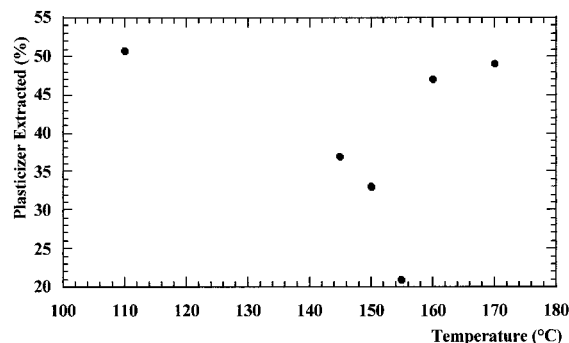

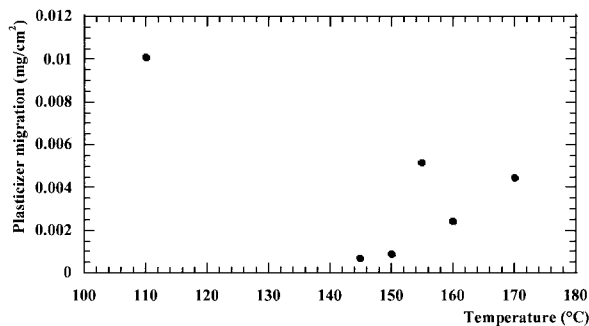**Figure 9** Hardness of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

Figure 11 Extraction of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

Figure 12   Migration of a PVC : Adilene-150 (100 : 60) plastisol at different cure temperatures (10 min).

Figure 14   Elongation of a PVC : Adilene-150 (100 : 60) plastisol at different cure times (150°C).

ture of PVC and they are easily extracted in supercritical conditions. A complete gelation, which corresponds to a minimum of the volume extraction, is obtained at 155°C. Above this temperature thermal degradation starts to play an important role and extraction of plasticizer is greater. This fact can be explained considering that, following degradation, some HCl molecules are evolved from the plastisol and some holes in the macromolecular structure of PVC permit an easier diffusion of additives and the removal of their molecules by the stream of the supercritical fluid.

A similar study was carried out for migration of plasticizer in such plastisols, the results of which are presented in Figure 12. As can be observed, migration is especially low for cure temperatures between 140 and 150°C, which corresponds with the extraction results previously presented. The amount of migrated material in these formulations is at least 10-fold lower than that exhibited in phthalates,[4] thus confirming the better environmental behavior of the new formulations. Therefore, from these studies a conclusion similar to that obtained with the study of mechanical properties
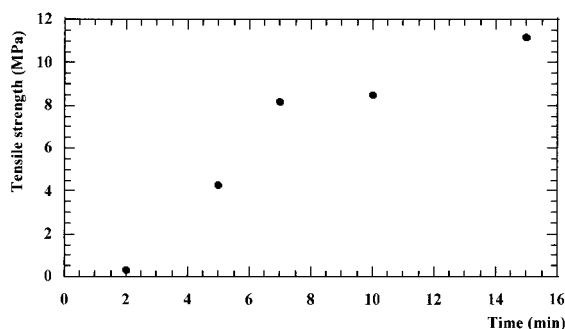
can be obtained, that is, the temperature range between 140 and 150°C is the optimum range for the cure of the plastisols here formulated.

Cure of Plastisols: Time

Time is the other parameter to be controlled for the optimization of the cure of plastisols. A similar study to that performed previously for the cure temperature was carried out with the measurement of mechanical and optical properties for different times between 2 and 15 min at 150°C. The selection of this temperature was made on the basis of the optimization of cure temperatures discussed earlier.

The variation of tensile strength versus time is shown in Figure 13. Three different regions can be observed, as in the case of temperatures: the first one with a clear increase in tensile strength between 2 and 6 min, a plateau between 6 and 10 min, and a slight increase for times higher than 10 min. A similar explanation indicated for the temperature effect can be applied in this case: an incomplete gelation is expected at times lower than 6 min and

Figure 13   Tensile strength of a PVC : Adilene-150 (100 : 60) plastisol at different cure times (150°C).

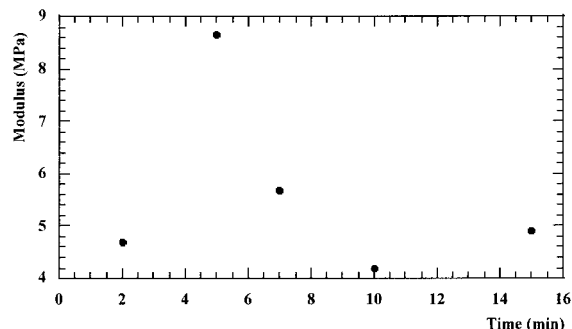**Figure 15**   Modulus of a PVC : Adilene-150 (100 : 60) plastisol at different cure times (150°C).

a beginning of thermal degradation at times higher than 10 min. A similar behavior is observed for the elongation at break of samples cured at different times, as shown in Figure 14.

As in the case of cure temperatures, the variation of hardness with time presents three stages, as shown in Figure 15. An increase is observed at low times, whereas a clear drop between 4 and 10 min confirms the completion of the gelation process. A slight increase is observed for higher times. A similar behavior of the variation of modulus with cure times is presented in Figure 16.

Finally, Figure 17 shows the variation of brightness of the cured plastisols versus time. A sharp drop is observed at times higher than 10 min, suggesting that at this time starts the degradation of the plastisol at 150°C.

CONCLUSIONS

New formulations of plastisols with the use of low-toxicity plasticizers have been proposed and mechanically characterized to assess their processability. The optimum conditions for cure were selected as 140°C and 10 min for a plastisol with a polypropylene–glicol adipate–based plasticizer (60 phr). Different concentrations of plasticizer were tested to obtain a formulation with properties similar to those exhibited by industrial PVC plastisols with phthalate plasticizer. It was indicated that the high viscosity is the main drawback of the innovative plastisols, although the addition of an auxiliary plasticizer with lubricant properties allows the obtainment of plastisols with viscosities similar to those exhibited in industrial materials.

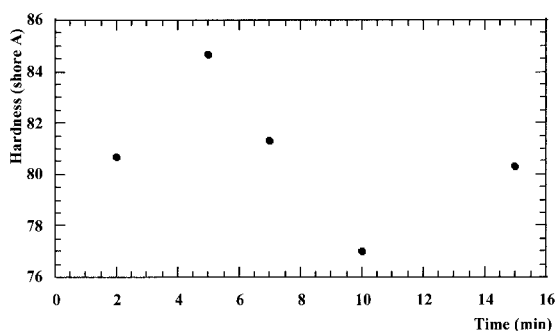The main objective of the present work was the use of low-migration additives to be used in PVC derivatives. The amount of migrated material in these formulations was determined to be at least 10-fold lower than that exhibited in phthalates. Therefore, the use of polypropylene–glicol adipate as an alternative to toxic additives in plastisols can be considered a promising possibility for the substitution of the industrial formulations currently under controversy.

Figure 17 Brightness of a PVC : Adilene-150 (100 : 60) plastisol at different cure times (150°C).

Figure 16 Hardness of a PVC : Adilene-150 (100 : 60) plastisol at different cure times (150°C).

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