Modification of Epoxy Resins by the Addition of PVC Plastisols

J. LÓPEZ,[1] S. GISBERT,[1] S. FERRÁNDIZ,[1] J. VILAPLANA,[1] A. JIMÉNEZ[2]

[1] Instituto Tecnológico del Juguete (AIJU), Av. Industria, 23, 03440, Ibi, Alicante, Spain

[2] University of Alicante, Department of Analytical Chemistry, P.O. Box 99, 03080, Alicante, Spain

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ABSTRACT: An epoxy resin based on bisphenol A has been modified by the addition of different amounts of a plastisol, based on poly(vinyl chloride) (PVC) and diethylhexyl phthalate (DOP). The fluid state of those materials makes their blending easier. After a curing process, some different materials, with properties ranging from the rigidity of a thermosetting resin to the flexibility of a plastisol, can be obtained. The variation of different parameters, such as tensile strength, Young's modulus, dielectric constant, and others, with the concentration of plastisol, has been studied. Some materials with properties similar to common thermoplastics (PP, ABS, or SB) can be processed, depending on the epoxy-to-plastisol ratio. The obtained results enable us the use of those materials in prototyping and other industrial processes. The obtained prototypes should have a similar mechanical behavior to thermoplastics. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1769–1777, 1998

Key words: epoxy resin; plastisol; mechanical properties; thermal behavior; blends

INTRODUCTION

Epoxy resins are essentially prepolymers that contain, on an average, two or more epoxide groups per molecule. They have been used in many fields, such as in flooring, composites, coatings, automotives and aircraft, but one of the most common uses of them is as a matrix for other materials by modification of some of their properties (thermal or electrical conductivity, hardness, etc).[1]

As epoxies are viscous liquids, their handling and conforming is relatively easy. There is a large variety of epoxy resins, depending on the kind of the curing agent. Those resins present very favorable physical properties, such as high Young's modulus, tensile strength, thermal stability, and good environmental resistance if they are compared with thermoplastics of general use. However, one of the major weakness of these materials is their brittleness or low fracture toughness.

There have been many research efforts over the last few years to improve the low toughness of the epoxy resins.[2–10] The most common procedure to toughen those brittle polymers is the blending of the epoxy resin with rubber with the result of an increase of the fracture energy of epoxies by an order of magnitude at least. However, the addition of rubber decreases clearly the modulus and yield strength of the epoxy.[11] Moreover, the toughness of an epoxy resin is inversely related to their crosslinking density.[10] Therefore, epoxies with high glass transition temperature and crosslink density are much more difficult to toughen by blending with rubber.

The use of thermoplastics has also been suggested in order to improve the toughness of a resin.[12] The most important improvement in

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Correspondence to: A. Jiménez.

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toughness is obtained at high fractions of the thermoplastic, where it becomes the continuous phase. Therefore, the best combination would be the addition of a liquid thermoplastic to the epoxy resin. Most of the modifications with reactive elastomers have been carried out using bifunctional epoxy resins derived from bisphenol-A. In the modification of such a highly crosslinked epoxy matrix, rubbers have been proved as ineffective modifiers. Therefore, the use of thermoplastics has been strongly recommended.

A very promising possibility to avoid some of the referred problems is the addition of a plastisol, which is a blend of a poly(vinyl chloride) (PVC) resin and a plasticizer, to the epoxy. The use of a plastisol as a toughening agent should considerably improve some properties of the epoxy resin. The plastisol contained in the blend should retain the impact with an increase of the energy absorbed during the fracture process. Therefore, by increasing the amount of the plastisol added, the brittleness should be highly reduced.

However, one problem arising from the use of a plastisol as a toughening agent comes from the fact that most of the applications of the epoxy resins are based on their good resistance to high temperatures. The low thermal stability of plastisols has been observed,[13] and a small decrease in thermal properties of the resulting product should be expected; but this should not be an important problem when using this new blend.

However, unlike the rubber-toughened epoxy materials, there is little known about the detailed relationships between the amount of thermoplastics added to the resin and the properties of the final product. The aim of the present work is the study of the behavior of the epoxy–plastisol systems in order to obtain materials with different mechanical properties for prototyping and vacuum casting. The relationship between different mechanical, thermal, and electrical properties with the amount of plastisol added will be studied.

EXPERIMENTAL

Materials

The epoxy resin used in the present work is based on the condensation reaction of bisphenol-A and epichlorhydrin (EPOSIER 7020, supplied by Sier, Spain). The curing agent was an amine type (END 0702, Sier). A PVC resin, Vestolit B 7021 (HULS, Germany), was mixed with a plasticizer, di-octil phthalate Vestinol AH (HULS) and a stabilizer Irganox 1076 (Ciba–Geigy, Switzerland) to obtain plastisols. Those components were mixed with a 100/70/2 ratio for PVC, DOP, and stabilizer, respectively. In addition, some other plastisols were prepared (100/50/2, 100/43/2, and 100/25/2) to study the effect of the plasticizer concentration in the blend. As they are not highly viscous liquids, their blending is relatively easy. Therefore, the use of an appropriate mixing machine with an strict temperature control to avoid undesirable curing and gelation is necessary. The epoxy-to-plastisol ratio used in the blends ranges from 0 to 400 parts per hundred resin (phr) of plastisol.

In order to know the stoichiometry of the epoxy–amine reaction, a differential scanning calorimetry (DSC) study was carried out as it was proposed in some previous works.[14–18] The variation in glass transition temperature (T_g) was obtained, and the maximum of the curve indicates the stoichiometry. In this case, a 100/16.5 ratio was obtained.

Equipment

A Brookfield viscometer B.V.II was used to determine the viscosity of the different blends. The variation in Young's modulus, elongation, and tensile strength was followed using an Instron 6000 machine with two different rates, 1 and 50 mm/min. The former was used to determine Young's modulus, and the latter to study tensile strength, with 4 × 8 mm samples. The impact energy absorption was measured with a Charpy machine when using 10 × 80 × 4 mm samples.

Thermal characterization of blends was performed using a Mettler TA 3000 instrument, which permits DSC, thermogravimetric analysis (TGA), and thermomechanical analysis (TMA) studies. Differential scanning calorimetry was used to determine the stoichiometric ratio for epoxy–amine blends and to study the release of heat in the cure of epoxy/plastisol blends. Temperatures were changed from 25 to 200°C with a 10°C/min increase. The start temperature of the TGA system was 25°C, and the end temperature was 800°C, with a temperature program of 20°C/min.

Finally, TMA was performed with a temperature program from 25 to 300°C with a 10°C/min heating rate. This technique gives information about expansion and softening of samples. The linear expansion coefficient for the epoxy resin and some samples not suffering any softening process was also determined.

To prepare the blends, a Brabender P-600 mixer coupled with a Brabender Plastigraph–Plasti-Corder register unit was used. This instrument was built according to German Standard DIN 54-802.

In order to obtain the electrical characterization of materials, a RLC Hewlett Packard coupled with a HP 1645B dielectric test fixture was used. The dielectric constant, or relative permitivity, has been measured for every sample, and the relationship between this parameter and the frequency was also investigated.

Blends of the epoxy resin and the curing agent were prepared according to Spanish Standard UNE 53-462-90, equivalent to ISO 4612-79, as well as epoxy–plastisol formulations. Thus, blends were prepared by mixing defined amounts of the resin, the curing agent, and the plastisol. Working conditions were as follows: temperature, 23 ± 2°C; rotation frequency, 120 min^{-1}; and mixing time, 20 min. The blend was then stored in a vacuum dessicator (7×10^{-2} Pa) to eliminate air. After a 2-h storing time, samples were ready for analysis. Samples for mechanical characterization were prepared by blending the epoxy and the plastisol, curing in rectangular molds (30 min, 120°C), and cutting them with an adequate tool to get the final sample.

RESULTS AND DISCUSSION

Some general properties of the different blends have been measured in order to know if the epoxy–plastisol mixtures could be considered as a good alternative to other formulations. The selected properties to be determined were viscosity; thermal properties, such as T_g; degradation temperature; mechanical properties, such as Young's modulus; elongation (%); tensile strength; hardness; and electrical properties.

Viscosity

The variation in the viscosity of the different epoxy–plastisol blends is shown in Figure 1. It can be observed that there is a general decrease in viscosity due to the action of the plastisol as a nonreactive diluent. If the concentration of the plastisol is higher than 60% (w/w), the blend presents a viscosity similar to the plastisol. This behavior is observed if a plastisol with high plasticizer content is used. As it is well known, diluents are employed in the epoxy technology primarily to reduce the viscosity of the mixture. As the diluent effect is caused mainly by the plasticizer, a decrease in the viscosity for blends with high plasticizer concentration should be expected.

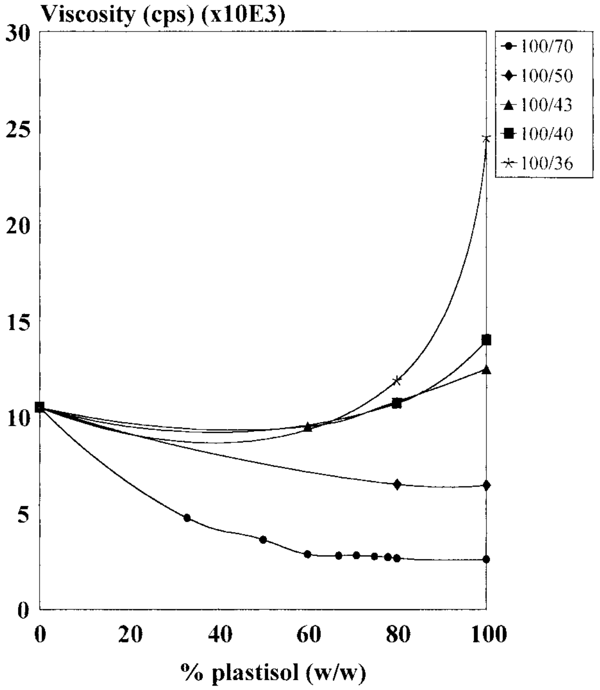

Figure 1 Viscosity of the epoxy–plastisol blends.

At present, there is not a general theory to explain the behavior of these blends. As it can be observed in Figure 1, the relationship is not linear; but all curves seem to fit a similar equation. As the epoxy–plastisol system may be considered as a nonNewtonian liquid, the viscosity could be determined taking into account the following equation.

$$\ln \mu = x_1 \ln \mu_1 + x_2 \ln \mu_2 + 2x_1x_2G \qquad (1)$$

where μ is the viscosity of the blend, μ_1 is the viscosity of the epoxy resin, μ_2 is the viscosity of the plastisol, x_1 is the % (w/w) of the epoxy resin, x_2 is the % (w/w) of the plastisol, and G is the parameter representing the interaction between the two components of the blend.

In this particular case, this parameter G can be calculated from the plasticizer concentration in the plastisol and the obtained results are presented in Table I. As can be observed, high plasticizer concentrations present low G values with a low interaction between the components of the

Table I ***G* Values of Some Plastisols**

DOP Concentration (phr)	*G*
36	−0.03
40	−0.07
43	−0.08
50	−0.31
70	−0.75

blend. Values of *G* are related to polarity of compounds. Plastisols are highly polar compounds, while epoxies present lower polarity.

Figure 1 also shows the viscosity curves for different plastisols. Therefore, the formulation of the plastisol presenting the same viscosity than the epoxy resin can be calculated. The obtained result is 100 PVC/43 DOP. These low values of viscosity allow the possibility of an easy handling and conforming by vacuum casting. However, if the viscosity of the plastisol is too high, the blend would be very stiff, and the handling of those materials would be very difficult.

Cure of Epoxy–Plastisol Blends

The cure of the epoxy–plastisol blends presents two main problems.[19,20] First of all, it is necessary to determine the minimum temperature to start the cure reaction of the epoxy resin. Otherwise, it is essential to reach the adequate temperature to get a correct gelation and/or fusion of the plastisol. TMA can be used to determine those temperatures. The use of thermocouples into the blend permits the adequate determination of cure temperatures. It is necessary to reach a temperature above 160°C in order to get a correct gelation and/or fusion of the plastisol. On the other side, epoxy resins cure even at room temperature with a highly exothermic reaction. Therefore, one fraction of the heat given off is used to maintain the epoxy resin temperature, a little fraction is released to the atmosphere, and the rest is absorbed by the plastisol.

In the present work, the temperatures used to get the cure of blends are as follows. Samples with plastisol concentration lower than 66.6% (w/w) have been cured at 120°C for 30 min. The heat released is enough to complete the two processes because the blend reaches a temperature higher than 160°C. Samples with plastisol concentration higher than 66.6% (w/w) have been cured at 140°C for 30 min. Figure 2 shows the variation of heat released in the cure process of epoxy–plastisol blends. The experimental curve represents the results obtained with different blends, while the theoretical curve represents the heat released in every case if we consider that the plastisol would only play the role of a diluent agent, with no reaction with the resin.

As can be observed in Figure 2, the two curves are very similar. This result means that the plastisol does not react with the resin during the cure reaction. The kinetics of the degradation of each component are independent with no interference between them.

Thermal Characterization

In order to know the thermal behavior of the epoxy–plastisol blends, a TGA study was carried out. The obtained results for every sample permit the determination of degradation temperatures and the influence of the plastisol concentration on them.[21,22] It has been reported that an epoxy resin suffers a complete degradation at temperatures above 350°C with decomposition of carbonated chains, while the degradation of PVC plastisols presents two different stages.[13] The first stage is

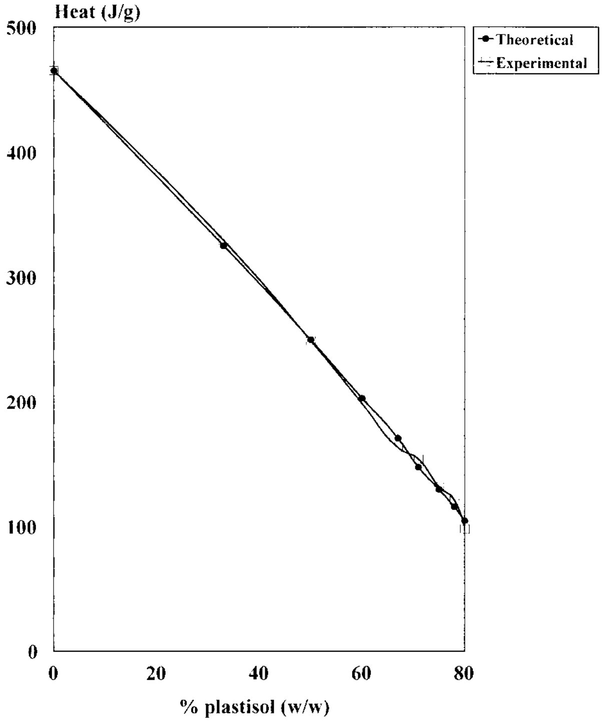

Figure 2 Variation of heat release in the cure of epoxy–plastisol blends.

Table II Degradation Temperatures of Different Epoxy–Plastisol Blends

% Plastisol (w/w)	T_1 (°C)	T_2 (°C)
0	348.9	377.0
33.3	283.4	336.7
50.0	263.9	285.2
60.0	249.3	281.7
66.7	264.6	285.4
71.4	268.5	285.0
75.0	267.5	285.9
77.7	273.2	293.1
80.0	272.3	293.0

observed at temperatures above 280°C and could be the result of two simultaneous processes, evaporation of plasticizer and PVC dehydrochlorination reaction, resulting in the formation of double C=C bonds. The second stage is observed at temperatures above 350°C with the pyrolysis of carbonaceous compounds previously formed.

The influence of the plastisol concentration in degradation temperature was studied. The results for onset temperature, T_1, and temperature of maximum weight loss, T_2, are indicated in Table II. The addition of a plastisol has the result of a decrease in degradation temperature due to the release of HCl and evaporation of plasticizer.

In addition, temperatures present a minimum value for 60% plastisol (w/w) with a small increase for higher concentrations. Therefore, those blends can bear temperatures as high as 180–200°C for a short time with no loss of general properties. However, it is recommendable to work at temperatures below 150°C to avoid the evaporation of the plasticizer and the beginning of the degradation.

The mechanical stability of the epoxy–plastisol blends is another important point to be studied. This study was carried out with TMA. It has been observed that epoxies suffer an expansion with temperature, while plastisols present a softening process previous to degradation with no enlargement. Samples with plastisol concentration lower than 66.6% (w/w) suffer an expansion because they are not penetrated by the instrument. Otherwise, concentrations higher than the referred, present the result of a softening of samples making them unuseful for prototyping. Therefore, one conclusion of the present study could be the knowledge of the recommended temperatures of use for every blend. Figure 3 shows the degradation, softening, and use areas for different blends.

Mechanical Characterization

The variation of some mechanical properties, such as Young's modulus, elongation, and tensile strength, was studied to get a complete characterization of the epoxy–plastisol blends.

The variation of tensile strength with the concentration of plastisol is presented in Figure 4. As can be observed, the addition of growing concentrations of the plastisol has the effect of a general decrease in tensile strength, with the blend becoming more flexible. The resulting material presents a small but significant plastic behavior very different from the elastic behavior presented by the epoxy resin.

Figure 4 shows some differences between blends with plastisol concentration. If it is lower than 66.6% (w/w), samples present an important decrease in tensile strength, while this is not very important for concentrations higher than the referred. As has been previously indicated, the epoxy matrix or the plastisol are the controlling material, conditioning the properties of the blend.

Young's modulus has been measured, and the results are presented in Figure 5. As can be observed, the graph is similar to the variation of tensile strength with plastisol concentration (Fig. 4). As is well known, the Young's modulus repre-

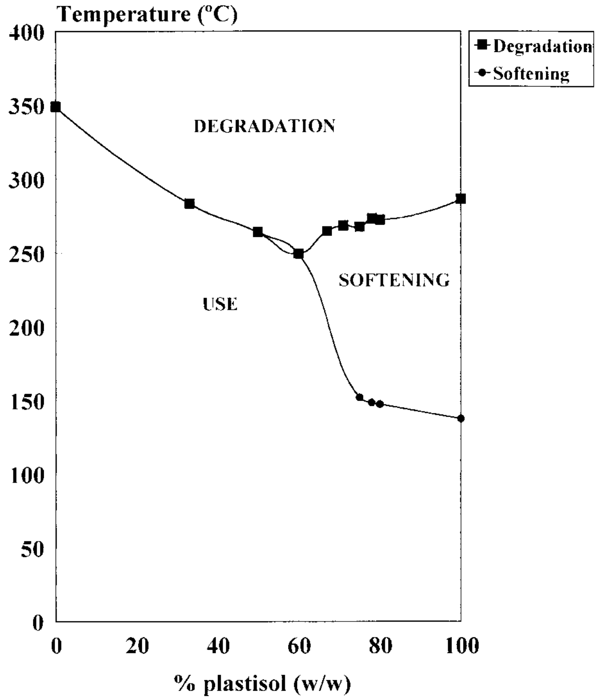

Figure 3 Degradation, softening, and use areas for epoxy–plastisol blends.

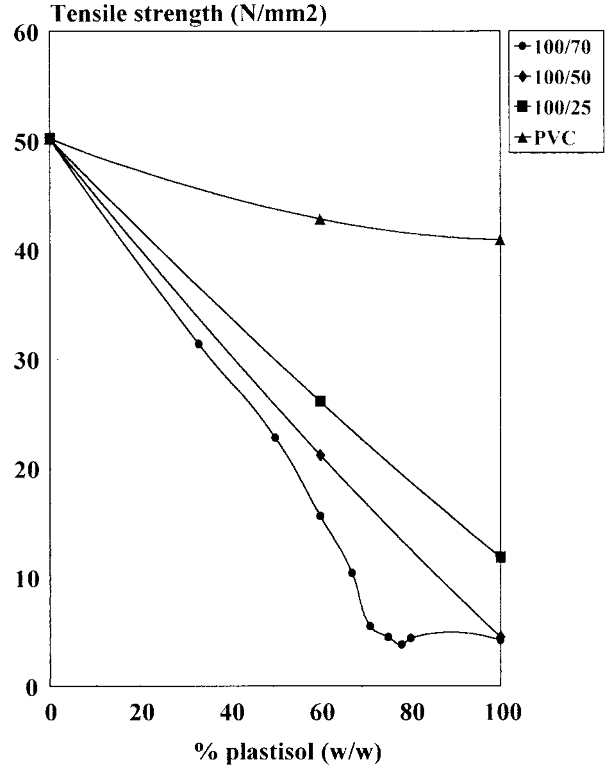

Figure 4 Variation of the tensile strength with plastisol concentration.

sents the relationship between tensile strength and elongation. When the modulus is high, the material is very resistant because it presents high strength and small elongation properties. Epoxies present a high resistance to traction, while this resistance is low for plastisols. Therefore, if the plastisol concentration is low, the Young's modulus should be high with an important decrease when this concentration is raised.

Figure 6 shows the variation of the percentage of elongation with the plastisol concentration. As should be expected, an increase in elongation is observed when plastisol concentration is higher. The reason of this behavior comes from the fact that plastisol presents polar bonds, permitting a significant movement into the chain. On the other side, epoxies have a three-dimensional structure with covalent bonds, and individual molecules are fixed to the net with no possibility of any important movement. Therefore, the addition of increasing amounts of plastisol lead to the insertion of some polar bonds into the net with the final result of a clear increase in elongation of blends.

A study was carried out to know the influence of the plasticizer concentration in the plastisol in the mechanical properties of the blend. As is indicated in Figures 4–6, when the plasticizer is used in low concentrations, plastisol increases the stiffness, and the movement caused by polar bonds is less important.

Impact Tests

The impact energy absorption was measured to know if the addition of a plastisol has the result of an increase in toughness of the blend. This parameter has been measured according to ISO-179 standard. It was observed that samples with plastisol concentrations lower than 66.6% suffered a rupture, while samples with concentrations higher than the referred did not break in any case because they were too flexible to be broken. Results are presented in Figure 7.

As it can be observed, there is an important increase in toughness, even when the plastisol concentration is not very high. This increase may be due to the influence of the plastisol in the mechanism of fracture. Molecules of plastisol in the blend act as soft points absorbing the impact. Those results mean that a big increase in versatility of the blends is obtained, as well as a clear

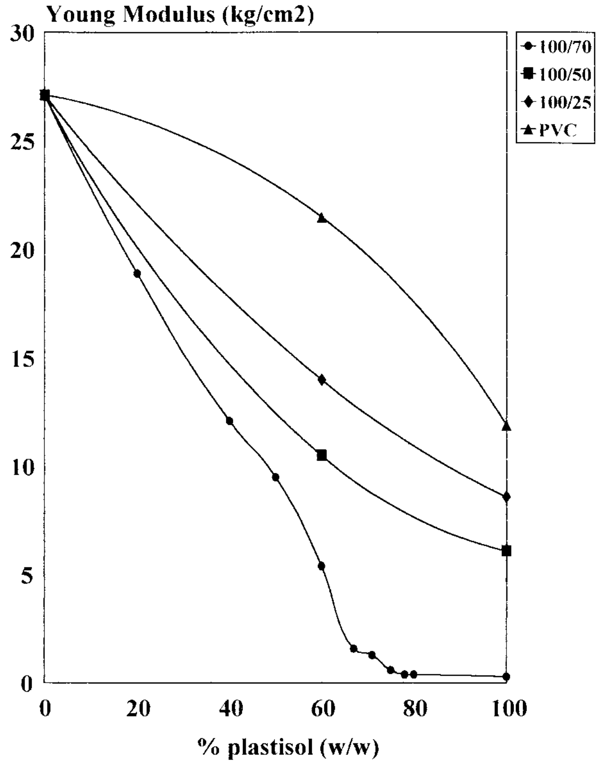

Figure 5 Variation of the Young modulus with plastisol concentration.

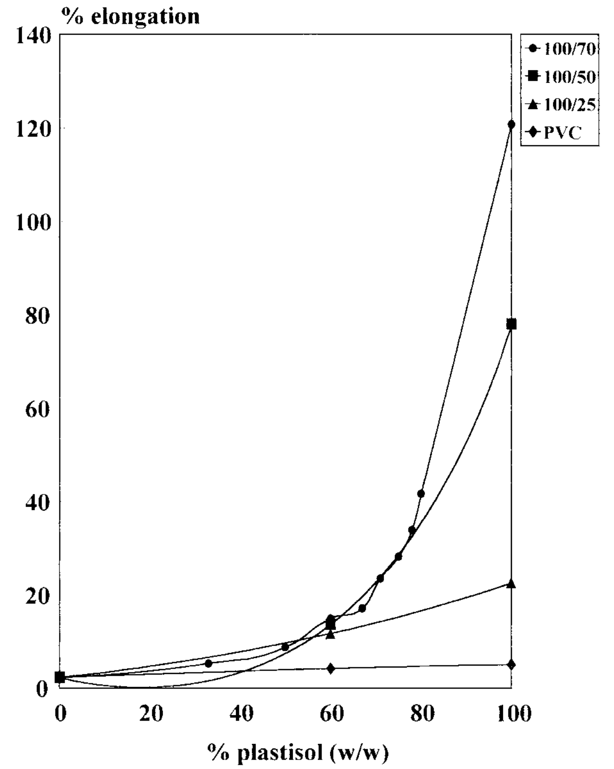

Figure 6 Variation of the elongation with plastisol concentration.

improvement in toughness and other mechanical properties. There are some other methods to improve toughness in epoxies, but the addition of plastisols could be one of the cheapest and most successful.

Hardness

This parameter was measured according to ISO-868 standard with the use of samples of 3 mm thickness. Figure 8 shows the variation of hardness Shore-D with the plastisol concentration. As can be observed, hardness results show a clear decrease from high values presented by epoxies to low values of plastisols due to the different bond structure of epoxies and plastisols. Thus, bonds between chains of PVC and molecules of DOP in a plastisol are dipoles. This structure permits some movement into the chains. The addition of a plastisol makes the density of covalent bonds in the epoxy lower, giving rise to a net with many polar forces and causing the observed decrease in hardness and other mechanical properties, as has been previously indicated.

However, it is well known that epoxy resins and PVC are reasonably compatible to form interpenetrating network structure (epoxy network and PVC crystallites). Therefore, some precaution must be taken into account when trying to explain the structure of cured products.

A clear change in the slope of the curve presented in Figure 8 can be observed for blends with plastisol concentration higher or lower than 60%. This fact can be caused by the above indicated differences in structure. Thus, when this concentration is lower than 60%, the obtained blend can be considered as a dispersion of a plastisol into an epoxy matrix, while the situation is reversed for plastisol concentrations higher than 60%.

Electrical Properties

The electrical characterization of the obtained materials was carried out by measuring the dielectric constant, or relative permitivity, which represents well the differences of electrical properties of various blends. The dielectric constant for different epoxy–plastisol blends and different frequencies (100 Hz, and 1, 10, and 100 KHz) was measured. Figure 9 shows the variation of the

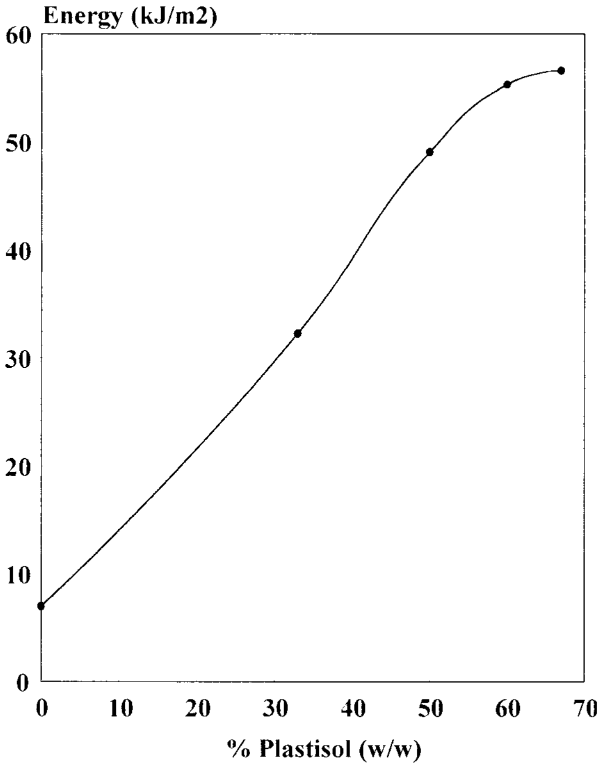

Figure 7 Variation of the absorbed energy with plastisol concentration.

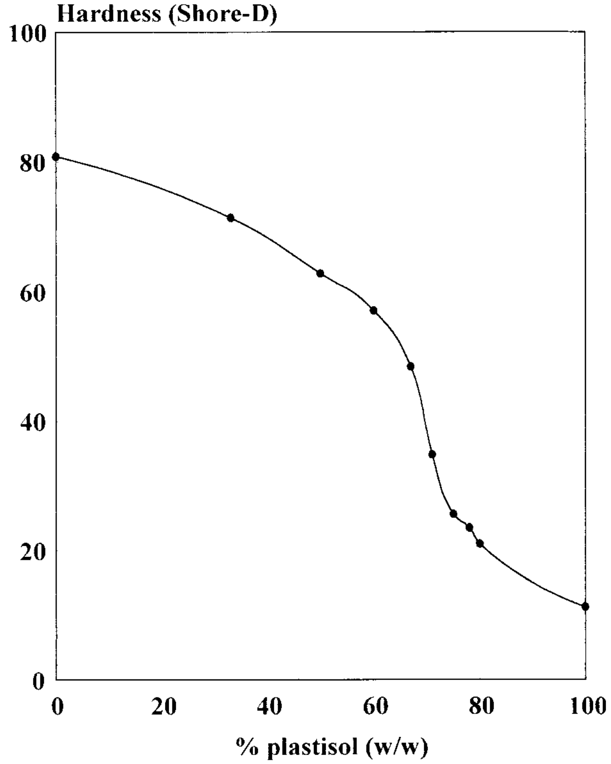

Figure 8 Variation of hardness with plastisol concentration.

dielectric constant as a function of the plastisol concentration, for a 100 Hz frequency. As can be observed, higher values for ε_r are obtained when the blend is richer in the plastisol. It may be due to the presence of a higher amount of polar groups in the plastisol structure coming from the contribution of C—Cl bonds and plasticizer dipoles. These dipoles can be orientated when an electric field is applied, and they are highly mobile. This permits a quick orientation with the result of an increase in the dielectric constant. The epoxy resin presents dipolar bonds too, but their mobility is lower because of the fixed structure of the thermosetting net.

The applied frequency is another important factor to be controlled when performing the electrical characterization. Figure 10 shows the variation of the dielectric constant as a function of the applied frequency. The dielectric constant can be considered as depending on many factors, such as frequency, temperature, moisture absorption, surface defects, etc. As can be observed in Figure 10, at low frequencies, the vast majority of dipoles can be orientated by the electric field with high values of ε_r. As the frequency increases, some dipoles cannot be orientated as fast as they were, and ε_r decreases. Therefore, the use of low frequencies when measuring the dielectric constant is recommendable because the differences when frequency is higher.

CONCLUSIONS

The new epoxy–plastisol blends have been characterized to know whether they may be used in some industrial processes, such as prototyping. The modification of the epoxy properties has been studied as a function of the plastisol concentration. Some mechanical, electrical, and thermal properties of the different blends have been measured. In addition, the viscosity of the obtained materials has also been determined to know if the use of those materials for vacuum casting and other industrial processes could present a general improvement in properties.

The main objective of the present work was the increase in the toughness of the epoxy resin. This increase can be measured by determination of mechanical parameters, such as tensile strength, Young's modulus, elongation, impact properties, and hardness. The addition of a plastisol leads to a

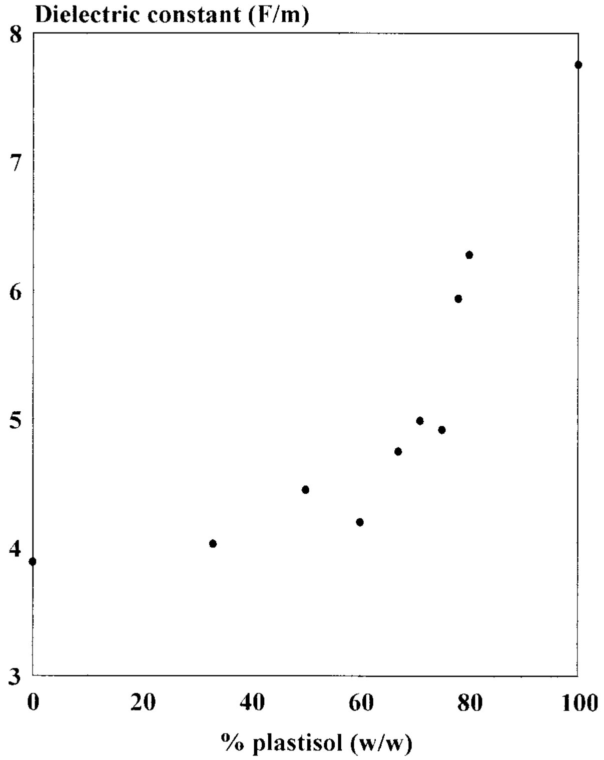

Figure 9 Variation of the dielectric constant with plastisol concentration.

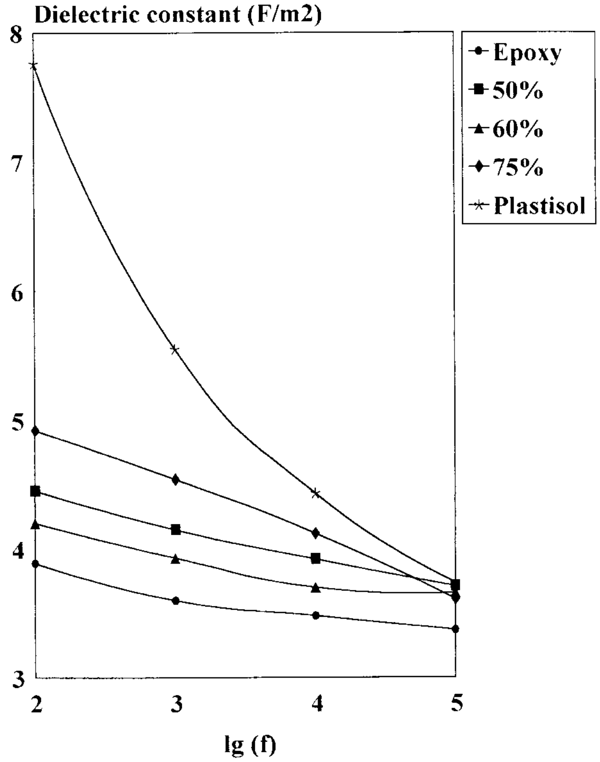

Figure 10 Variation of the dielectric constant with the applied frequency.

decrease in Young's modulus and tensile strength. Otherwise, elongation and absorbed impact energy increase considerably. The epoxy-to-plastisol ratio should be chosen depending on the foreseen use of the final product.

The thermal analysis of different cured samples has shown an improvement on the thermal stability, presenting a degradation and a softening area, but with an important range of use conditions. A study of the variation of the dielectric constant of the epoxy–plastisol at different frequencies has been also carried out.

As a final conclusion, the proposed epoxy–plastisol blends have shown as a resistant, versatile, and cheap material for prototyping, making them a promising raw material to be used in industry.

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