Substitution of Di(2-ethylhexyl) Phthalate by Di(isononyl) Cyclohexane-1,2-Dicarboxylate as a Plasticizer for Industrial Vinyl Plastisol Formulations

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ABSTRACT: The use of plasticizers with low environmental impact is one of the most interesting research fields in the plasticizer additives industry because of the possible toxicity of *o*-phthalates. Among the wide variety of new plasticizers, it is important to note the use of di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH), which shows a structure similar to the most commonly used *o*-phthalates, that is, diisononyl phthalate and di(2-ethylhexyl) phthalate (DEHP). It is necessary to evaluate the processing conditions (temperature and curing time) regarding the mechanical properties to study the possibilities for substituting conventional plasticizers and to determine whether changes in the processing conditions are needed for use in industrial applications. In this work, we car- ried out a comparative study of the optimum curing conditions and mechanical performance of DEHP and DINCH as plasticizers. The obtained results show that the viscosities of DINCH and DEHP-based plastisols were similar. Furthermore, the mechanical properties of the flexible poly(vinyl chloride) obtained from DINCH-based plastisols were very interesting for industrial applications. All of this favored the substitution of DEHP by DINCH as plasticizer for flexible poly-(vinyl chloride). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1215–1220, 2007

Key words: curing of polymers; mechanical properties; poly(vinyl chloride) (PVC); viscosity

INTRODUCTION

Phthalate plasticizers, such as diisononyl phthalate and especially di(2-ethylhexyl) phthalate (DEHP), are common plasticizers widely used in industrial applications. The latter is the most commonly used in the industrial sector; nevertheless, its use is being questioned because of its possible toxicity due to plasticizer migration.[1–3] Thus, alternative plasticizers and different blends[4,5] are being investigated[6] to ensure low migration in applications that are particularly sensitive to it.[7–12] These plasticizers, based on the use of benzoates, trimellitates, citrates, sebacates, carboxylates, and so on,[13–16] represent interesting alternatives as substitutes for traditional phthalates, and most of them are based on the use of low-toxicity additives and biodegradable components. Despite this, they are not widely used in industrial applications.

In this new group of plasticizers, we find carboxylates, in particular di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH).[17] This plasticizer is obtained by the hydrogenation of the benzene ring that is present in *o*-phthalates, and this process enables its use in medical devices and in the toy industry (Fig. 1).[18]

Both DINCH and DEHP show similar molecular weights but present some structural differences.[18,19] The main difference is the flat structure of the benzene ring as opposed to the typical chair structure of cyclohexanes. This different structure can strongly affect the plasticizer–poly(vinyl chloride) (PVC) interaction process. In this work, we carried out a comparative study of the main parameters affecting the process at the industrial level (viscosity) and the effect of the curing conditions on the final performance of cured plastisols; the formulations covered the typical values used in rotational molding in the 30–80-phr range.

EXPERIMENTAL

Materials

The PVC resin Lacovyl PB 1172 H was supplied by Atofina (Atofina UK, Ltd., Midlands, United Kingdom) with a kwert (k) value of 67 obtained by ISO 1628-2, which was suitable for rotational molding. Two different plasticizers were used for the comparative study. The plasticizer used to analyze the influence of the curing conditions of PVC plastisols was a carboxylate type, DINCH (HEXAMOLL DINCH) developed by BASF, Ltd. (Cheshire, United Kingdom). Some properties were compared with a phthalate plasticizer, DEHP supplied by Sigma Aldrich
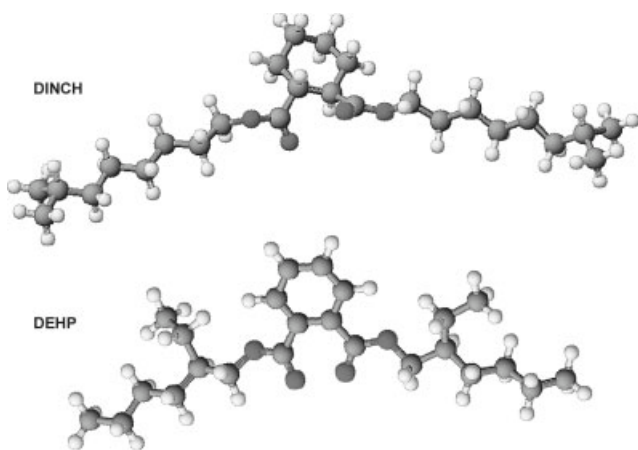
Figure 1 Schematic three-dimensional representations of DINCH and DEHP.

(Dorset, United Kingdom), with a high level of purity that was close to 99%.

All plastisol formulations included 2 phr of the stabilizer Vinstab H-6 supplied by Hebron S. A. Industrias Químicas y Farmacéuticas (Barcelona, Spain), which was based on Ca–Zn.

Equipment and procedure

We prepared the plastisols by mixing adequate proportions of PVC resin, plasticizer, and stabilizer in a rotative mixer KAPL mod. 5KPMS (KAPL, St. Joseph, MI). After the mixing process, the pastes were subjected to a vacuum process for 30 min in a MCP Group vacuum chamber model 00ILC (HEK-GmbH, Lübeck, Germany) with a maximum vacuum of −1 bar. Once all of the air bubbles were removed, we determined the viscosity of all the plastisols with a Ford cup following the guidelines described in ASTM D 1200 with a snapout orifice 4 mm in diameter by determining the time needed to empty the cup. After the vacuum process, plastisols with different compositions were spread into an aluminum mold.

The curing process of the plastisols was performed in a ventilated oven Carbolite mod. 2416CG (Keison Products, Barcelona, Spain) with a maximum temperature of 300°C. Curing times and temperatures were varied in the range 3–12 min and 160–220°C, respectively. Sheets 190 × 140 × 4 mm in size were obtained after the curing process in an aluminum mold. These sheets were stamped in a die on a hydraulic press (MEGA KCK-15A, Melchor Gabilondo S. A., Vizcaya, Spain).

The mechanical properties of the plastisols were determined with a universal test machine (Ibertest Elib 500, Ibertest, Madrid, Spain), which was able to measure tensile strength, elongation at break, and modulus in a single experiment as described in ASTM D 638 with an elongation rate of 50 mm/min. Samples were used with no prior treatment, and probes were prepared with an adequate tool to obtain the final standard

shape (4 × 8 mm rectangular samples specially prepared for the test). Shore D hardness was measured with a Baxlo durometer (Baxlo, Barcelona, Spain) with samples 3 mm thick according to the standard defined in ASTM D 2240. At least five measurements were carried out, and average values were calculated.

RESULTS AND DISCUSSION

In this study, we followed a methodology that was useful in industrial processes, and we focused on the formulations and curing conditions commonly used in rotational molding processes.

Viscosity of the system

Before the curing process study, we evaluated the influence of the type and plasticizer content on the viscosity response of the plasticizer–PVC system, and we observed some differences associated with the plasticizer nature and aging of pastes as described by other authors with similar systems.[20–22] Pastes elaborated with DINCH as the plasticizer showed lower viscosity values than pastes obtained with DEHP; this was evident for the whole composition range evaluated. Importantly, at room temperature, DINCH showed a lower viscosity (42–52 P) than DEHP (100–130 P). Nevertheless, these differences were relatively small and did not involve important changes in the processing conditions.

There are several models to predict the viscosity behavior of a plastisol; some of them, based on the simple suspension model, do not fit well for low concentration ranges. Better results are obtained with other models that assume more complexity in the plastisol structure. Ram and Schneider proposed the following simplified empirical expression:

$$\eta_r = A \, \exp\left[\frac{BW}{1 - W/W_p}\right] \qquad (1)$$

where η_r is the apparent viscosity of the plastisol, A and B are empirical constants, W is the weight fraction of the polymer, and W_p is the critical weight fraction (defined as the weight fraction to gel when the viscosity rises to high values).

The concept of critical weight [strictly, the critical volume (ϕ_c)] was also used by Johnston and Brower to develop one of the expressions that better describes the relationship between η_r and its suspension fraction. This expression was validated for different plasticizer–resin systems, and it is independent of particle size changes and distribution. This expression is as follows:

$$\log_{10} \eta_r = \left(1,33 - 0,84\frac{\phi}{\phi_c}\right)\left(\frac{\phi}{\phi_c - \phi}\right) \qquad (2)$$

The application of the two models allowed us to consider the following: we observed that both models fit
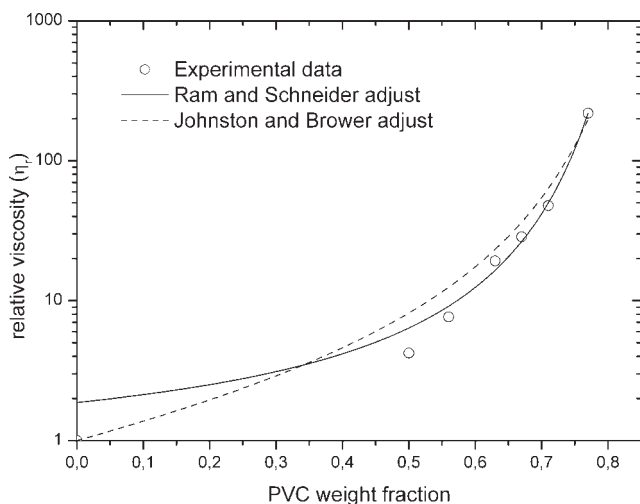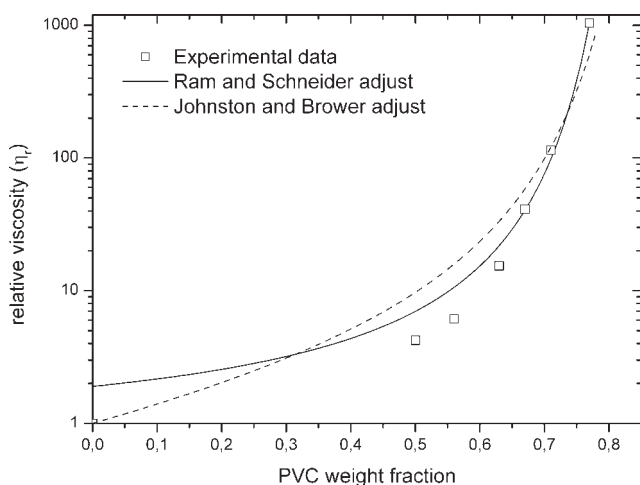
Figure 2 Evolution of the relative viscosity in terms of the weight fraction and adjustment to the Ram and Schneider and Johnston and Brower models for the DINCH–PVC system.

the experimental results accurately, as shown in Figures 2 and 3, but the most important aspect was the good agreement with the critical volume (ϕ_c) values in both models (Table I).

The higher ϕ_c value for DINCH in comparison to DEHP indicated a lower plasticizer interaction, and this was also observed when the aging times were evaluated for the different pastes. We easily observed that pastes based on DINCH were less sensitive to the aging phenomenon in the short term, and in a 15-day period, no increase in viscosity was achieved (Fig. 4).

Mechanical properties. Influence of time and curing temperature

The optimum curing conditions of vinyl plastisols require a balance between two variables, temperature

Figure 3 Evolution of the relative viscosity in terms of the weight fraction and adjustment to the Ram and Schneider and Johnston and Brower models for the DEHP–PVC system.

TABLE I
ϕ_c Values for the Ram and Schneider and Johnston and Brower Viscosity Models and for Different Plasticizers

| Model	DINCH	DEHP
Ram and Schneider	0.92	0.85
Johnston and Brower	0.91	0.86

and curing time;[23,24] it is absolutely necessary to select an appropriate temperature and curing time to ensure a complete curing process because it is the key factor in obtaining good mechanical properties. Short curing times are interesting from an industrial point of view because they allow a considerable increase in productivity, but they require the use of high curing temperatures to accelerate the process. On the other hand, excessive exposure to high temperatures may induce degradation processes because PVC is especially sensitive to thermal degradation. It is possible to obtain optimum processing conditions by following the evolution of the mechanical properties as a function of the curing temperature and time; this method is also an interesting tool for gaining a deeper knowledge of gelation processes because it provides information about the appropriate temperature needed to obtain a cured plastisol independently of its curing time. This study was carried out with a plasticizer content of 50 phr and by analysis of the mechanical properties of different samples (at different curing times and temperatures).

In the plot of the evolution of mechanical properties (Figs. 5 and 6) as a function of the curing temperature, we observed that logically, the system reached optimum properties at shorter curing times. The minimum curing time needed for an optimum curing process at 200°C was approximately 5 min; these processing conditions (220°C and 5 min) are common in the industrial processing of vinyl plastisols, even with the use of different plasticizers. The experimental results show that it was convenient to reach temperatures above 165°C to obtain cured plastisols with good properties within a practical length of time. This was associated with the internal structure of PVC because it could reach certain levels of crystallinity; then, it was necessary to reach a certain critical temperature to induce the melting process of PVC crystallites.[23]

These processing conditions will allow DINCH-based plastisols to be processed in a way similar to phthalate-based plastisols. This represents an important advantage in replacing phthalate plasticizers with lower toxicity plasticizers such as DINCH.

Effect of plasticizer addition

Apart from the variables described previously (curing temperature and time), another important variable to
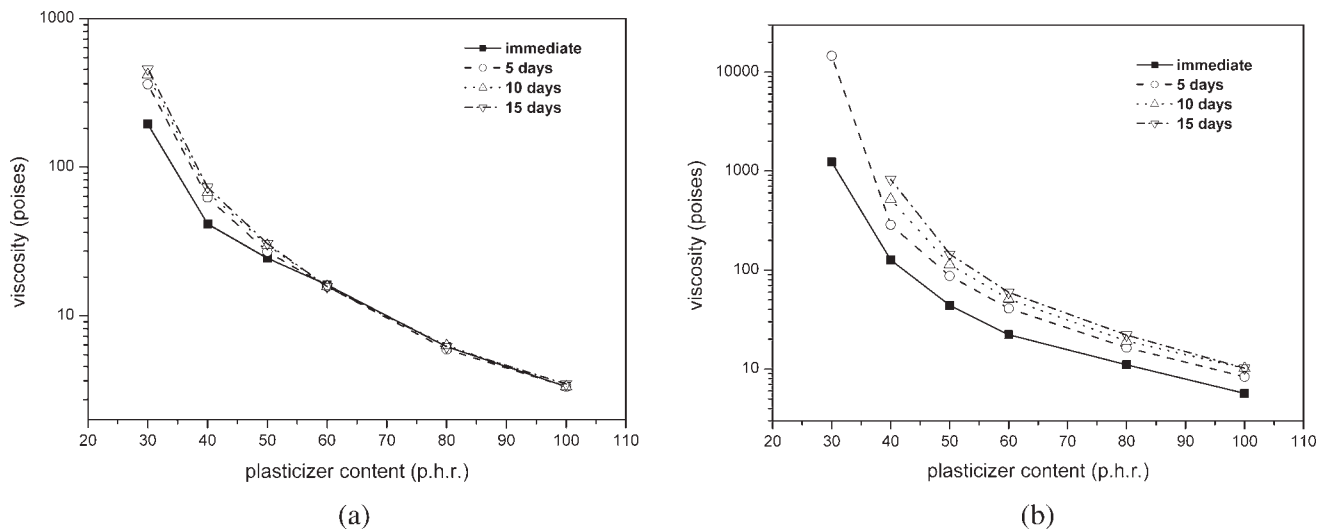
Figure 4 Evolution of the viscosity for pastes elaborated with different plasticizer contents (2 phr of stabilizer Vinstab H-6) and effect of the aging time on (a) DINCH–PVC and (b) DEHP–PVC systems.

be considered in the final performance of vinyl plastisols is the plasticizer content, not only in absolute terms but also in terms of the plasticizers to be replaced, especially of DEHP because this material, widely used in industry, is considered as a reference, and frequently, the behavior of new plasticizers is compared with it. For this reason, the mechanical properties of the flexible PVC obtained from the DINCH- and DEHP-based cured plastisols was measured in a wide range of plasticizer contents (30–100 phr) under the same curing conditions (200°C and 9 min). By comparing the effects of plasticizer addition on the tensile strength and elongation at break, we observed that flexible PVC based on DINCH and DEHP cured plastisols showed similar tensile strength

values for the entire study range, but DINCH plastisols were much more flexible, and they showed higher elongation at break values than those obtained with DEHP (Figs. 7 and 8). Furthermore, in both cases, plasticizer contents higher than 80 phr did not greatly influence the mechanical properties, especially elongation at break; therefore, it was possible to consider this content as the maximum plasticizer content that could be added to a PVC resin and cause significant changes in PVC performance.

We also observed higher Shore D hardness values for flexible PVC obtained from DINCH-based cured plastisols, which was indicative of higher cohesion levels in the cured material (Fig. 9); but this behavior was only noticeable for low plasticizer contents. As we observed, in the low hardness range, both materi-
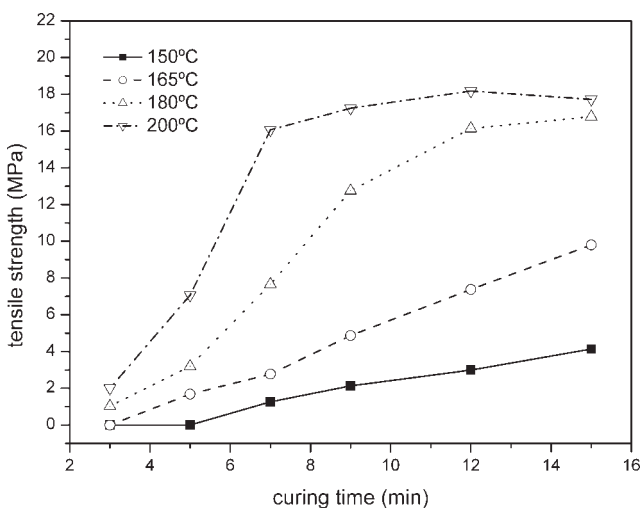

Figure 5 Variation of the tensile strength as a function of the curing time at different temperatures for a plastisol formulation of 50 phr DINCH.
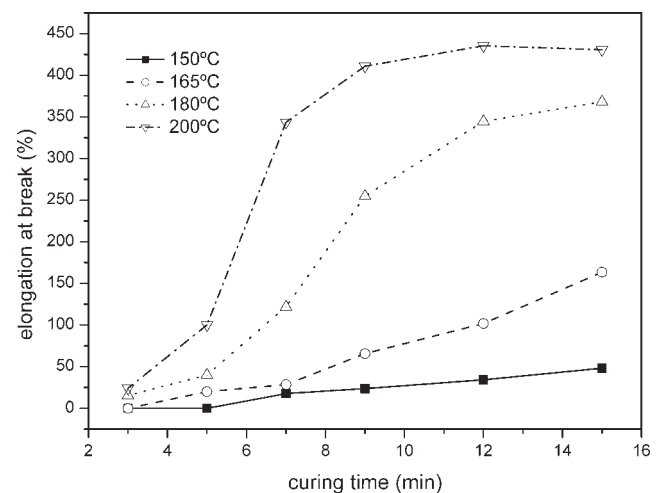
Figure 6 Variation of the elongation at break as a function of the curing time at different temperatures for a plastisol formulation of 50 phr DINCH.
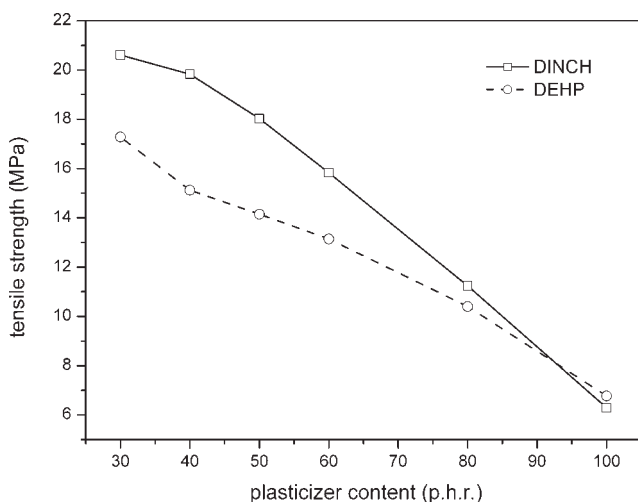
Figure 7 Variation of the tensile strength as a function of plasticizer content for DINCH and DEHP (curing conditions: temperature = 200°C and time = 9 min).
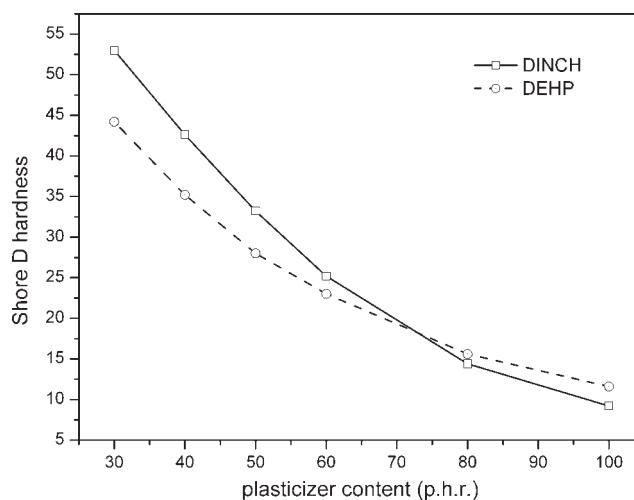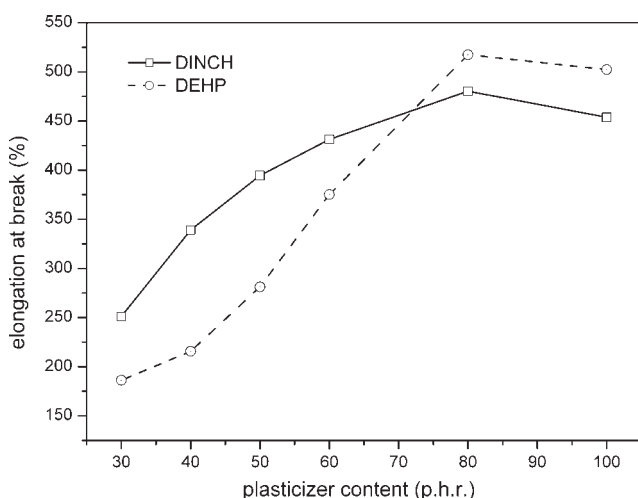

Figure 9 Variation of the Shore D hardness as a function of plasticizer content for DINCH and DEHP (curing conditions: temperature = 200°C and time = 9 min).

als showed similar behaviors, and similar hardness values were achieved with similar plasticizer contents in both DINCH and DEHP. Nevertheless, for low plasticizer contents, flexible PVC from DINCH-based plastisols showed higher Shore D values than DEHP-based plastisols. This was a disadvantage, but it was only appreciable for low plasticizer contents. Because many industrial applications require plasticizer contents in the range 50–70 phr, it would not be a problem to substitute DEHP in plastisol formulations. These differences in mechanical performance were better observed in the analysis of tensile energy absorption (TEA; measured as the area below the stress–strain curve) in both materials. This indicates the cohesion achieved and can be considered a variable that includes not only resistant properties (tensile strength)

but also ductile properties such as elongation at break. We observed that DINCH-based plastisols showed higher TEA values than those obtained with DEHP, although this behavior was similar for formulations in the range 50–80 phr (Fig. 10). These plasticizer contents are the most widely used for rotational molding products, such as toys, so no significant differences in the use of either DEHP or DINCH plasticizers should be appreciated.

CONCLUSIONS

Our comparative analysis, developed with a traditional industrial plasticizer (DEHP) and a new carboxylate plasticizer (DINCH) with low toxicity, indicated that both plasticizers showed similar viscosities for

Figure 8 Variation of the elongation at break as a function of plasticizer content for DINCH and DEHP (curing conditions: temperature = 200°C and time = 9 min).
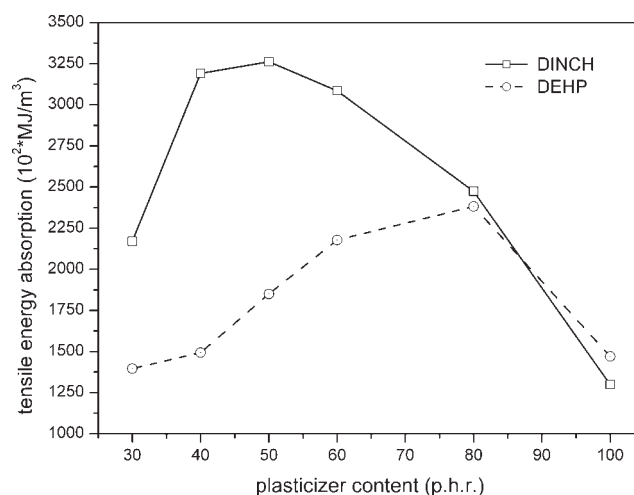
Figure 10 Variation of TEA as a function of plasticizer content for DINCH and DEHP (curing conditions: temperature = 200°C and time = 9 min).

the formulations used in rotational molding, so the substitution of DEHP for DINCH should not require important changes in the plasticizer content or even the use of viscosity modifiers for use under similar processing conditions.

In a similar way, for DINCH-based plastisols, we observed that the main curing parameters used in rotational molding (curing time and temperature) fit in the typical range values for this technique: curing temperatures close to 200°C and curing times in the range 5–10 min. Furthermore, as with other plasticizers, it was necessary to reach a critical temperature value (ca. 165°C) because lower temperatures did not ensure a complete curing process, even with longer curing times.

Finally, some differences in the mechanical properties of DINCH and DEHP plastisols were observed. DINCH-based plastisols showed better behavior than DEHP-based plastisols for low plasticizer contents, but in the typical range used in rotational molding (50–70 phr) for toys, no significant differences between the two plasticizers were appreciated, and they were perfectly exchangeable.

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