Soft PVC Foams: Study of the Gelation, Fusion, and Foaming Processes. I. Phthalate Ester Plasticizers

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ABSTRACT: The use of foamed plastics gains more and more interest every day. Flexible poly(vinyl chloride) (PVC) foams have excellent mechanical properties and low price, thus their application is extensive. Foams are produced from plastisols, which are based on the suspension of the PVC resin in a plasticizer. Phthalates are the most used plasticizers in flexible PVC foam formation. In this study, we have studied the influence of the phthalate ester-type plasticizers on the foaming process and the quality of the foams obtained from the corresponding plastisols. For the plastisols prepared with the nine phthalate plasticizers considered, we have studied and discussed the complex and extensional viscosities; the thermal behavior (DSC) including the decomposition of the chemical blowing agent, and the foam production by rotational molding. In addition, we have characterized the foams obtained by thermomechanical analysis, density, and bubble size distribution. As expected, clear correlations have been obtained between the molecular weight and structure of the plasticizer with the rheological behavior of the plastisols. The knowledge of the gelation and fusion processes and evolution of the extensional viscosity of the plastisols combined with the study of the thermal decomposition of the blowing agent in each plastisol allows for better understanding of the complex dynamic behavior of these foaming systems. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1495–1505, 2011

Key words: phthalates; flexible PVC foam; characterization

INTRODUCTION

The use of polymer foams is extremely widespread in all kinds of different applications. They can be manufactured from many different types of polymers and there are many different additives—such as plasticizers, stabilizers, chemical blowing agents, kickers, etc. —available to customize the foam to specific requirements. Excellent properties such as light weight, low density, outstanding strength/weight ratio, superior insulating abilities, and energy absorbing performance make polymer foams especially attractive. Packaging, biomedicine, building, automotive, carpet underlay, textiles, furniture, as well as the production of toys are some of the main areas of use of polymer foams.

According to their cell geometry, foams can be open-cell or closed-cell. In general, the open-cell foams are flexible while the closed-cell ones are rigid.[1–3] This fact can change due to the glass transition temperature (T_g) of the resin, which in turn depends on the chemical composition, the degree of crystallinity, and the degree of crosslinking. Good melt strength (i.e., the maximum stress before a rupture of the samples in the extensional tests occurs) is also fundamental to produce a foamed plastic. Amorphous resins such as poly(vinyl chloride) (PVC) have good melt strength; however, melt strength-enhancing additives are commonly used to improve foaming and make cellular PVC with lower densities and better cell-structure.[4] Generally, higher melt strength with larger expansion ratio can be achieved by rising molar mass, as the cell walls of a material with the higher melt strength are able to withstand larger pressures before they break. The failure of a cell wall causes faster diffusion of the blowing agents through the foam therefore leads to an accelerated gas loss. Besides the melt strength, the strain hardening behavior of the system plays a dominant role for foaming.[5]

The unique physical, mechanical, and thermal properties of foamed thermoplastics are governed by the polymer matrix, characteristics of the cellular structure (e.g., cell density and cell size), and the bowling agent (BA) composition.[6] To generate thermoplastic foams, dissolved gas molecules have to be converted into bubbles through cell nucleation and growth. Cell nucleation occurs when the system pressure drops below a critical pressure, called the solubility pressure. Once nucleated, cells continue to

grow until they are either stabilized by cooling or ruptured by overstretching.

Foams are produced in a number of different ways such as extrusion and different types of molding. Rotational molding[7] is widely used in flexible PVC foam production, for example for toy applications. This process generally occurs at elevated temperatures, and involves the curing of a plastisol and the releasing of the gases from the decomposition of the chemical blowing agent (CBA). Furthermore, gelation and fusion processes and the development of the melt strength have to be synchronized with the evolution of the gas to enable the polymer matrix to withstand the stresses involved and stabilize the foam structure.

The foaming of a PVC plastisol is slightly different from the foaming of a thermoplastic polymer such as polystyrene or polypropylene. The main differences are the structural changes undergone by the paste during heating and the nature of the blowing agent system.

Plastisols are suspensions of fine particles of PVC resins in a plasticizer,[8] including thermal stabilizers and other additives.[9] When heated, plastisols undergo different processes. At a certain temperature the plasticizers start the swelling of the polymer particles and the viscosity of the sample starts to increase. On further heating, the swollen particles interact with each other and a process known as gelation takes place. Such process continues provoking a marked increase in the viscosity. At higher temperatures, the fusion process[10–12] (the PVC crystallites fuse and the system forms a homogeneous material) takes place. After all these transformations, the sample has developed its final structure as a polymer solution and its viscosity decreases with the increasing temperature. In the process of gelation, a liquid suspension of PVC resin with plasticizer becomes a solid material with elastomeric properties.[13] The evolution of the rheological properties of the system during its processing strongly depends on the effects of the plasticizers and other additives. Accordingly, the final product obtained may have different mechanical and physical properties. The measurement of the viscoelastic properties of the polymer matrix by oscillatory tests has been widely used for studying such effects.[10,14–19]

In a plastisol foaming system, the nucleation of the bubbles is produced by the decomposition of the CBA. Such decomposition is accelerated by the presence of the ZnO or other additives. The bubble growth and the final foam structure depend on the operating conditions, the rate of the CBA decomposition and the properties of the matrix.

Calorimetry is also a very useful method for plastisol characterization, as well as to study the decomposition of the blowing agent[20] involved in this type of processes. Glass transition, melting and exothermic decompositions involve changes in energy or heat capacity, which can be detected and easily followed by differential scanning calorimetry (DSC). In previous works, we studied the DSC behavior of different PVC plastisols and the kinetics of the transitions in the thermal treatments of polymers,[21] binary mixtures of polyethylene (PE) and ethylene vinyl acetate (EVA) copolymer[22] and ternary foamable mixtures of EVA, PE, and the CBA azodicarbonamide (ADC).[23] Other DSC studies of PE and EVA were also carried out, and a kinetic model was suggested.[24] Important effects and interactions among the different components of the formulations were observed including also the crosslinking process.[22,25–28]

Thus, in the case of flexible PVC foam production, the processes of gelation and fusion of the plastisol must be adequately synchronized with the process of the decomposition of the CBA to obtain good-quality foams. This can be achieved by the proper selection of the adequate plasticizer for the plastisol formulations, so that the required balance of properties is obtained in the final product. Different plasticizers can be used; however, phthalates are the most popular considering that more than 3.5 million tons of phthalates are used worldwide each year in flexible PVC production.[9,29] Dioctyl phthalate (DOP) is the most frequently used plasticizer; nevertheless, its use has been questioned because of its environmental and health implications, which have been the cause of several European regulations for special applications.[30] A further related issue that is very important to consider is the migration of the plasticizer,[31,32] diisononyl phthalate (DINP) and other plasticizers have been used and developed as substitutes of DOP. All these facts make it very interesting to study the capability of alternative plasticizers used in foam formulations.

Consequently, the objective of this study is to study the effect of several linear and branched commercial phthalate ester plasticizers on the rheology of the corresponding plastisols, the decomposition of the blowing agent, as well as the properties of the foams obtained, to attain a better understanding of the complex dynamic behavior of these foaming systems.

EXPERIMENTAL

Materials

Plasticizers

Nine commercial phthalate ester plasticizers were selected to prepare plastisols of PVC (with 5% vinyl acetate) to carry out this study. Table I shows the plasticizers selected, the abbreviation, the commercial name, the density, and molecular weight as well as the manufacturer.

TABLE I
Plasticizers Selected

Plasticizer	Abbreviation	Commercial name	Density (g/cm^3)	Molecular weight (g/mol)	Supplier
Linear					
Diethyl phthalate	DEP	Palatinol A	1.118	222	BASF
Heptyl nonyl undecyl phthalate	HNUP	Palatinol 711-P	0.971	418	BASF
Nonylundecyl phthalate	NUP	Palatinol 911-P	0.958	450	BASF
Diundecyl phthalate	DUP	Palatinol 11	0.953	475	BASF
Branched					
Diisobutyl phthalate	DIBP	Palatinol IC	1.039	278	BASF
Diisoheptyl phthalate	DIHP	Jayflex 77	0.991	362	Exxon
Diethylhexyl pthtalate	DOP	Palatinol DOP	0.983	391	BASF
Diisononyl phthalate	DINP	Palatinol N	0.973	421	BASF
Diisodecyl phthalate	DIDP	Palatinol DIDP	0.966	447	BASF

PVC resin

In a preliminary study of the resin to produce soft foams, ETINOX 400 PVC-EVA copolymer provided the best flexible foam with an appropriate bubble size distribution. Thus, PVC resin ETINOX 400 by AISCONDEL (which is a vinyl chloride-vinyl acetate copolymer with a nominal 5% of vinyl acetate, typical values provided by the supplier are 4.8% of comonomer and a K value of 70) was used to prepare these plastisol formulations.

Reagents

CL4 Commercial Ca/Zn stearate by REAGENS and Lankroflex 2307 epoxidized soybean oil by AKCROS CHEMICALS as stabilizers, zinc oxide by PAN-KREAC as kicker, and azodicarbonamide (ADC) D 200 A by UNICELL as chemical blowing agent were used.

Methods

Plastisol preparation for rheological measurements, DSC, foam production and foam characterization

Nine PVC plastisols were prepared by mixing 100 phr (parts per hundred resin) of ETINOX 400 from AISCONDEL, 100 phr of one of the nine phthalate ester plasticizers, 2 phr of Reagens CL4 commercial Zn/Ca-stearate stabilizer, 6 phr of Lankroflex 2307 epoxidized soybean oil as costabilizer, and 2 phr of zinc oxide. After mixing, the pastes were subjected to a degassing process for 15 min with a maximum vacuum of −1 mbar for air removal. These plastisols (not including the foaming agent) were used to study the rheological properties of the polymer matrix (i.e., in the complex viscosity and the extensional viscosity measurements). For DSC measurements, foam production and foam characterization, 2 phr of chemical blowing agent (azodicarbonamide) was also added to the same plastisol formulations.

Rheology experiments

Bohlin CS 50—Complex viscosity measurements. Gelation and fusion processes were studied by measuring complex viscosity by oscillatory tests between 40 and 180°C with a 5°C/min heating rate using 20 mm diameter parallel plates with a gap of 0.5 mm, oscillation frequency of 1 Hz, and controlled deformation of 5×10^{-3}, in a Bohlin CS 50 rheometer. *Advanced rheometer expansion system—Extensional viscosity measurements.* The extensional viscosity of 10 mm × 18 mm × 1 mm samples, previously cured at 180°C for 10 min, were measured at 160, 170, and 180°C, at each temperature applying three different prestretch rates (i.e., as 0.1, 0.5, and 1 s^{-1}) and at each condition applying five different extensional rates (i.e., 0.1, 1, 5, 10, and 15 s^{-1}) using the Extensional Viscosity Fixture Accessory.

Differential scanning calorimetry measurements

Thermal transitions of the plastisol, including the decomposition of the ADC were studied in a Perkin–Elmer Pyris 6 DSC between 40 and 220°C at 5°C/min heating rate in nitrogen atmosphere with a 20 cm^3/min flow at 20°C.

Foam production by rotational molding

To obtain the corresponding PVC foams by rotational molding, the following conditions were applied:

Plastisols were poured into a 5-cm diameter 10 cm length cylindrical mold and placed into the Roto-speed RL 1-400 rotational molding machine. First cycle (curing) occurs at 210°C for 8 min with a 10 : 2 rpm arm: wheel speed ratio, while second cycle (cooling) involves 2 min airflow, 10 min water flow, and finally 2 min airflow.

Determination of the foam density

To measure the foam density, Mettler-Toledo Density Kit for Analytical Balances was used. Appropriate
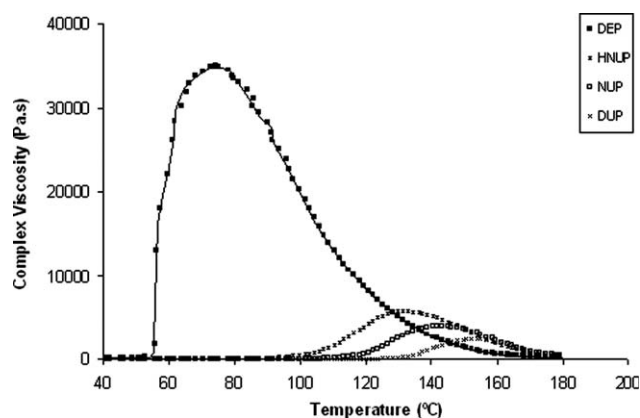
Figure 1 Evolution of complex viscosity (Pa s) with temperature (°C)—linear chained phthalates.

sampling is crucial, thus all the foam samples were cut out from the most homogeneous part of the entire foam, and replicated samples were measured.

Determination of the bubble size distribution

To determine the bubble size distribution, including the mean bubble size and standard deviation, photographs of the cross section of the foam parts prepared were taken and analyzed. Using various imaging programs (GIMP, Image J, Paint, Photoshop), reliable results were obtained for the average radius and the standard deviation of the corresponding distributions.

Thermomechanical analysis measurements

To determine thermomechanical properties such as penetration resistance of the foam, a Setaram 92-16.18 TMA instrument was used. Two cycles of heating were applied: the first heating cycle between 30 and 100°C at 5°C/min heating rate in nitrogen atmosphere without applying force; and the second heating cycle between 30 and 100°C at 5°C/min heating rate in nitrogen atmosphere with a 0.04-N force applied.

RESULTS AND DISCUSSION

For better, this section has been organized in two parts, i.e., plastisol characterization and foam characterization. In the first part rheological and calorimetrical behavior of the plastisol formulations, while in the second part the complete foam characterization will be discussed.

Plastisol characterization

As the main objective was to study the influence of the molecular weight, structure, and compatibility of

the plasticizer in the foam formation and the quality of the final foam obtained, knowledge of the rheological behavior of the plastisol matrix is very important.

Rheology

Evolution of the complex viscosity determined by dynamic oscillatory tests—Bohlin rheometer. For the sake of clearness the results obtained will be presented separately. Figure 1 shows the temperature dependence on complex viscosity for plastisols prepared with linear chained phthalate ester plasticizers, while Figure 2 shows the corresponding data for branched chained phthalates. In these formulations the blowing agent was not included to avoid the foaming in the measuring system.

All the curves obtained exhibit typical behavior for this type of material. After the initial reduction of viscosity with the temperature corresponding to the initial suspension, the viscosity markedly increases as a consequence of the interactions between the particles of the resin and the plasticizer, and at a certain temperature the gelation process starts to take place. The solvation,[33] swelling[34–36] of the resin, and fusion processes occur upon further heating. These processes have been widely described in the literature.[11,37–40]

Depending on the plasticizer type and compatibility with the PVC resin and the rate of applied heating, these interactions start at different temperatures and the various phenomena can be identified as a series of slope changes on the complex viscosity/temperature curve.[41,42] Beyond a certain temperature, where these phenomena no longer occur, the viscosity of the sample undergoes a continuous diminution with temperature. This behavior is typical of a melted sol polymer whose properties become fully developed at the higher temperatures. The slope of the viscosity/temperature curve of these materials is determined by the molecular weight of the final solution.[43]
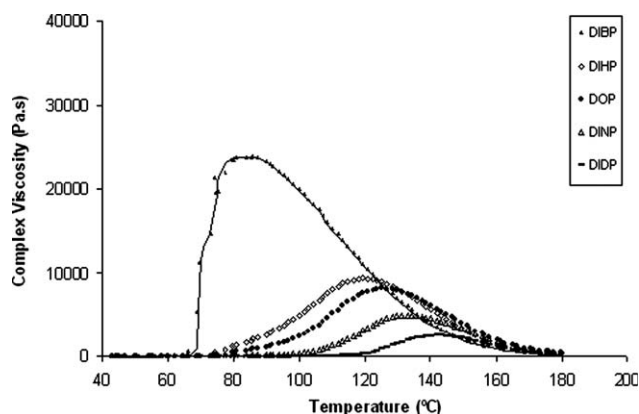

Figure 2 Evolution of complex viscosity (Pa s) with temperature (°C) —branched chained phthalates.
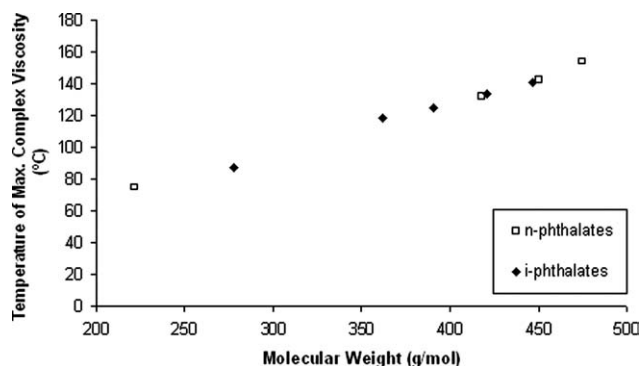
Figure 3 Temperature of maximum complex viscosity (°C) versus molecular weight (g/mol).

Figure 4 Maximum complex viscosity (Pa s) versus temperature of maximum complex viscosity (°C).

In the present case, most of the curves present a single and wide maximum in the complex viscosity/ temperature curve. This behavior is typical for the high plasticizer concentration used in this study. In a previous work[38] by our group, the influence of the plasticizer concentration on the rheology of such plastisols was studied. It was observed that the increase in the plasticizer concentration resulted in less pronounced initial processes (gelation) that were almost unobservable at the higher concentrations; however, the curves exhibited a single maximum and a decrease in the viscosity of the plastisols developed. In this study, only curves for the most compatible plasticizers (DEP and DIBP) show such shoulders at the beginning of the viscosity increase which corresponds to the gelation of the resin.

It must be emphasized that gelation of the formulations prepared with DEP and DIBP occurs at lower temperatures and develops higher viscosities than the rest of those studied. This fact is a consequence of the high compatibility of these plasticizers that interact in a very effective way with the PVC resin at the early stages of the process at lower temperatures. For this reason, their maximum viscosities are remarkably higher than for the rest of the plasticizers of this family.

Nevertheless, at elevated temperatures the viscosities of these two plasticizers decrease with temperature more than the rest of the plasticizers. This is because these plasticizers have the lowest molecular weight of each group. Viscosity values have found as functions of the molecular weight and structure of the plasticizer[14,37,44,45] at high temperatures when gelation has already taken place. All these facts are very important when studying the foaming of these formulations since the decomposition of the foaming agent must be adequately synchronized with the properties of the paste being foamed.

Figure 3 shows the temperature of maximum complex viscosity versus the molecular weight for both families of plasticizers. It can be observed that all of them follow the same linear behavior that could be
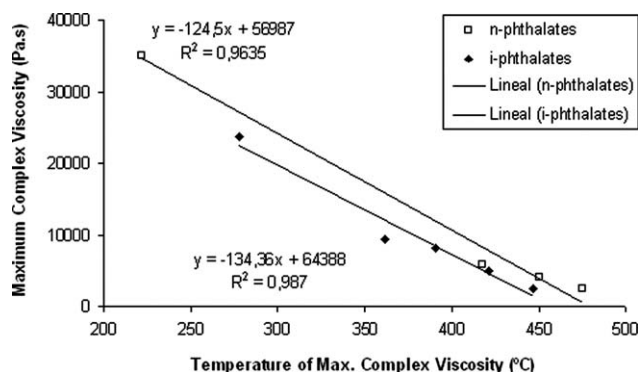
represented by a single straight line with a positive slope. Figure 4 shows the maximum viscosity attained by each plastisol at the corresponding temperature. In this case the same linear behavior could be deduced, but the two families seem to group in two different straight lines with similar slopes but different y-axis intercepts, which are lower for the branched phthalates. In other words, for the same molecular weight a branched phthalate would develop a lower maximum viscosity than the corresponding linear phthalate.

The influence of the degree of development of the structure of the plastisol can be clearly observed in Figures 5 and 6, where the complex viscosities of the linear and branched chained phthalates are shown at 140 and 170°C versus the molecular weight of the plasticizer. At 140°C, not all the plastisols have fully developed their structure, only those which are prepared with less molecular weight plasticizers. For this reason, and as expected, plastisols prepared with higher molecular weight plasticizers do not follow the increasing trend of the already fused plastisols. However, at 170°C most plastisols show the expected increasing trend, since at this temperature most of them have already finished developing their new properties and structure.
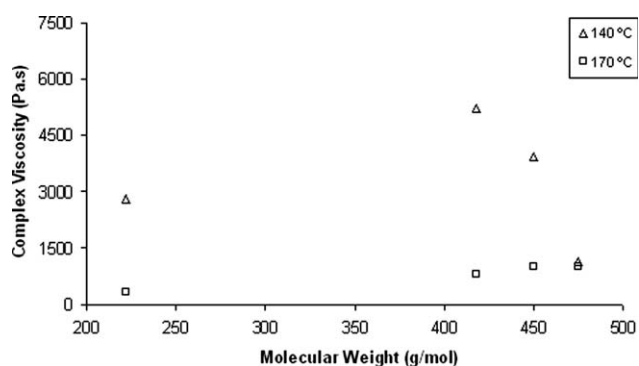

Figure 5 Complex viscosity (Pa s) versus molecular weight (g/mol) —linear chained phthalate ester plasticizers.
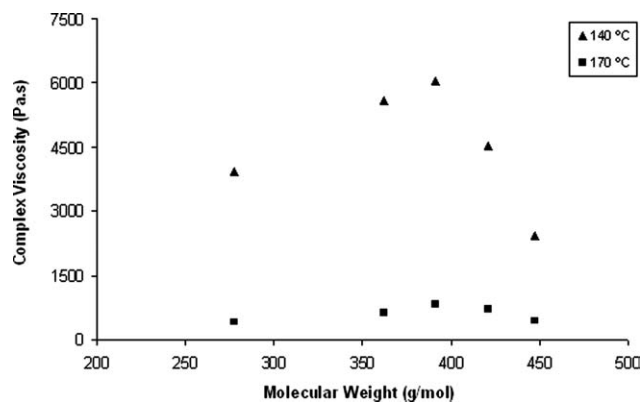
Figure 6 Complex viscosity (Pa s) versus molecular weight (g/mol)—branched chained phthalate ester plasticizers.

Figure 8 Extensional viscosity (Pa s) versus time (s) at 170°C—linear chained phthalate ester plasticizers.

Consequently, not only is knowledge of the complex viscosity at the moment of the gas generation important, but also the state of the plastisol regarding its fusion process has to be considered to understand the behavior of the plastisols in the foaming process.

This behavior is clearer in the case of the linear phthalates, where only the NUP slightly departs from the straight line defined by the others at 170°C. In the case of the branched phthalates, there are two plasticizers (DINP and DIDP) that still depart from this trend.

Extensional viscosity measurements—ARES rheometer. According to the literature, knowledge of the evolution of the extensional viscosity of the plastisols is considered as an important factor when studying the foaming process of plastisol formulations and other polymers.[46–51]

For this reason, in this article the influence of the plasticizer type on the extensional viscosity of the plastisols was also studied to characterize the plastisol matrix. As in the previous case, the CBA was not added to avoid the foaming in the extensional viscosity measurements. A series of measurements with
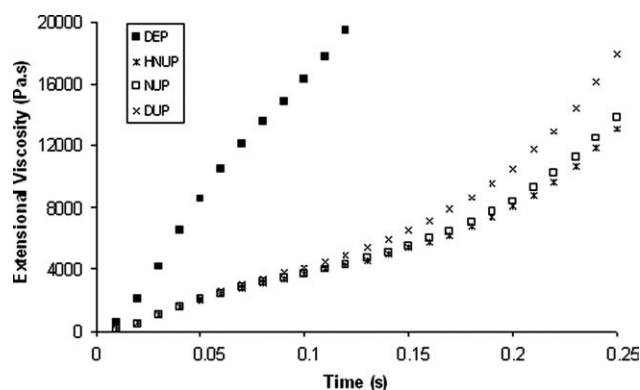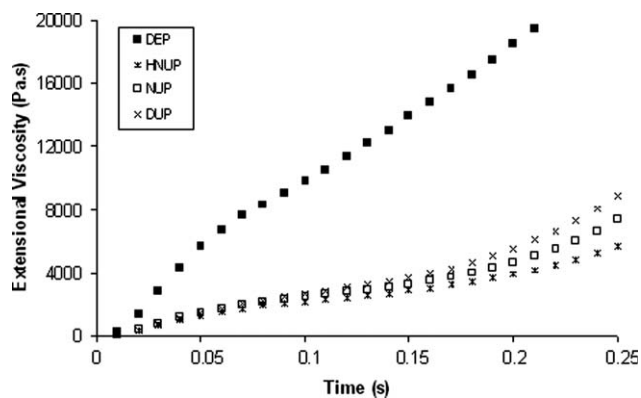
different conditions were carried out as explained in the experimental section.

Figure 7 shows the evolution of the extensional viscosity of the linear chained phthalates at 160°C measured at 0.1 s^{-1} prestretch and a 5 s^{-1} extensional rate. It can be emphasized that DEP, which has the lowest molecular weight, shows the highest slope and presents elevated viscosities in shorter time than the other plasticizers studied. This can be explained taking into account the higher compatibility of DEP and its more effective way of interaction with the PVC. The other three plasticizers studied present similar behavior among them.

Figures 8 and 9 show the evolution of the extensional viscosity of the linear phthalates at 170 and 180°C under the same conditions. It can be observed that all plasticizers follow the same trend. The influence of the molecular weight of the plasticizer in extensional viscosity is not as clear as in the case of the complex viscosity. DEP shows the largest extensional viscosities at the three temperatures studied. Contrarily to the case of the complex viscosity, that once fusion has been completed, the higher molecular weight plasticizers present the higher viscosities. The extensional viscosities of the rest of plasticizers
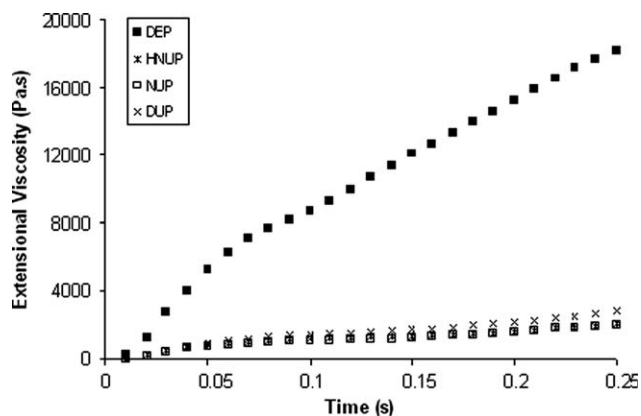

Figure 7 Extensional viscosity (Pa s) versus time (s) at 160°C—linear chained phthalate ester plasticizers.
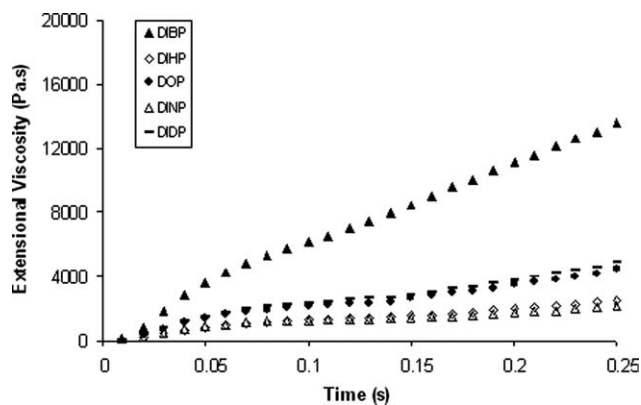

Figure 9 Extensional viscosity (Pa s) versus time (s) at 180°C—linear chained phthalate ester plasticizers.

Figure 10 Extensional viscosity (Pa s) versus time (s) at 160°C—branched chained phthalate ester plasticizers.

Figure 11 DSC of plastisols with linear chained phthalate ester plasticizers.

follow similar behavior with the molecular weight as described for the complex viscosity, the higher molecular weight plasticizer showing the higher extensional viscosity. The exceptional case of DEP could be related to the development of the final structure of this plastisol. The formulation prepared with DEP may have fully finished developing its final properties in the first treatment (180°C for 10 min), whereas the other plastisols prepared with lower plasticizing capacity plasticizers may be not fully cured.

On the other hand, and as expected the extensional viscosity decreases with temperature. The shear thickening seems to also decrease with temperature, which is in good agreement with the results reported by Sugimoto et al.[52] when studying the rheological properties of PVC/plasticized systems and the relation with elongational viscosity.

Figure 10 shows the results obtained in the case of the branched phthalates at 160°C, similar graphs were obtained at 170 and 180°C. It can be observed that branched phthalates show very similar behavior to the linear phthalates. The DIBP shows a similar early increase (although less pronounced) of the extensional viscosity to that observed in the case of DEP. As in the case of the complex viscosity, the extensional viscosity of the branched phthalates is lower than for the linear ones.

Calorimetric behavior determined by DSC

Figures 11 and 12 show the heat flow in arbitrary units versus the temperature for the plastisols prepared, in this case containing the blowing agent. In general, it can be observed that all these curves show two main peaks. The first one at about 60–80°C, which is probably due to the glass transition temperature (T_g) of the resin, and the second one at about 140–160°C which is the decomposition temperature of the chemical blowing agent (T_{ADC}). Peña et al.[53] observed the T_g of the unplasticized ETINOX
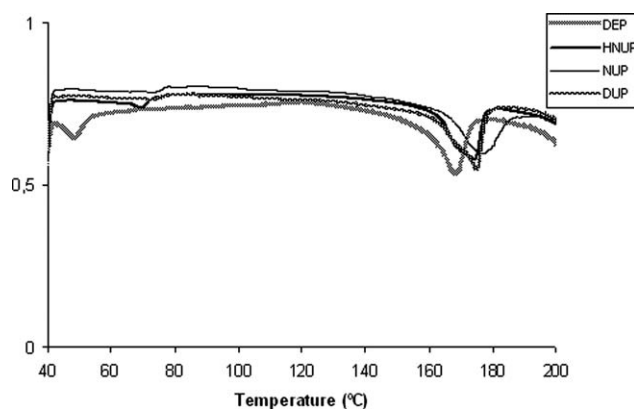
400 resin at 81.7°C, and a transition process at temperatures below this T_g.

According to these results, it can be emphasized that the first process appears mostly as an exothermic peak and this could be attributed to the T_g of the PVC-VA copolymer appearing at lower temperatures than that corresponding to the T_g of the copolymer without plasticizer. Furthermore, it is also greatly affected by the nature of the plasticizer. The second process that always appears as an exothermic peak clearly corresponds to the decomposition of the ADC. It is strongly influenced by the type of plasticizer and its molecular weight.

Further aspects such as the width of the second peak, corresponding to the ADC decomposition at T_{ADC}, as well as the starting temperature, must also be discussed, and not only the peak temperature of this process. These three parameters are important, since the foaming process must be adequately synchronized with the viscosity evolution of the plastisol to obtain good quality foams. However, two samples with the same peak temperature may lead to foams of very different quality when in the first one the ADC decomposition starts much earlier
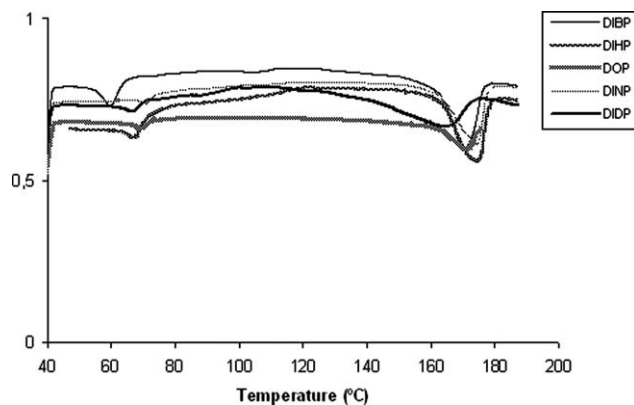

Figure 12 DSC of plastisols with branched chained phthalate ester plasticizers.
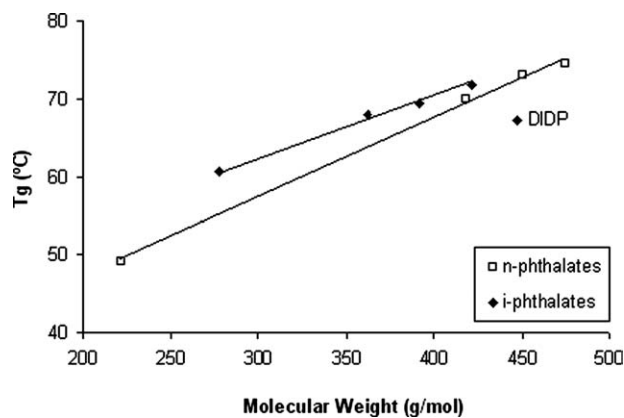
Figure 13 T_g (°C) versus molecular weight (g/mol).

Figure 14 T_{ADC} (°C) versus molecular weight (g/mol).

than in the second. It could be that at low temperature the structure of the first paste is still not fully developed, thus the sample could not withstand the pressure developed by the releasing gases.

It is worth mentioning how type and molecular weight of the corresponding plasticizer affect the T_g and T_{ADC}. Figure 13 shows the T_g against the molecular weight of the plasticizer in the case of the linear and branched phthalates. It can be observed that the temperature corresponding to the first process increases with the molecular weight. This is probably a consequence of the fact that plasticizers of lower molecular weight are more compatible with the PVC resin; and consequently at a given temperature the polymer chains have more mobility thus making the transition observable at lower temperatures. From the point of view of the structure of the pastes and their rheology, such transitions occur before the gelation process, or in its early stages where the resin might still be in the suspension stage or somewhat swollen. An exception can be found in the case of the DIDP (Fig. 13) that presents temperatures much lower than that corresponding to the approximately linear correlation observed for the rest of the phthalates studied. Comparing the linear and branched phthalates (except for the DIDP), it can be observed that, for the same molecular weight the T_g is somewhat higher in the case of the branched plasticizers showing a lower plasticizing capacity, i.e., modifying to a lower extent the T_g of the resin. This fact is in good agreement with the previously observed effect in the maximum complex viscosity.

Figure 14 shows the ADC decomposition temperatures (T_{ADC}) against the molecular weight of the plasticizer. In this case, similar trends can be observed; i.e., the second peak temperature increases in most cases with the molecular weight. However, a larger dispersion can be observed for the higher molecular weight plasticizers, especially in the case of the DIDP that clearly departs from the mentioned trend. In this case, a very wide peak with an early
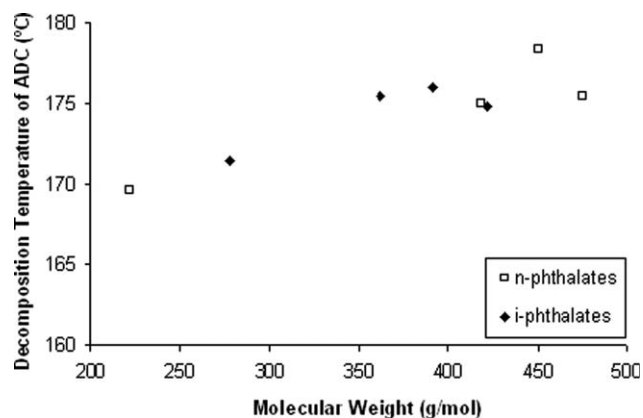
start is observable. No explanation has been found for this special interaction of this plasticizer with the ADC, but the presence of an impurity is possible. Moreover, this formulation leads to poor quality foam, which is also distinct from the other plasticizers but shows the importance of knowledge of the thermal and rheological behavior of the pastes to explain their foaming behavior.

Foam characterization

In this section of this article, the results of foam density, morphology of the foams, bubble size distribution, and TMA results are presented to characterize the final foamed product and discuss the influence of the plasticizer type on the foam formation and quality.

Thermomechanical properties by TMA

Considering the experimental procedure followed in preparing the foams, all foams would present the similar values of the nominal density, since the mold is closed, filled with the same amount of plastisol, and open when cold. Nevertheless, the foams obtained are very different in quality; many of them show very good uniformity whereas others show

TABLE II
Measured Foam Density of the Final Foam

Plasticizer	Measured foam density (g/cm³)
Linear	
DEP	0.343
HNUP	0.278
NUP	0.328
DUP	0.342
Branched	
DIBP	0.311
DIHP	0.319
DOP	0.333
DINP	0.318
DIDP	0.563

Figure 15 TMA curves of foams prepared with linear chained phthalate ester plasticizers.
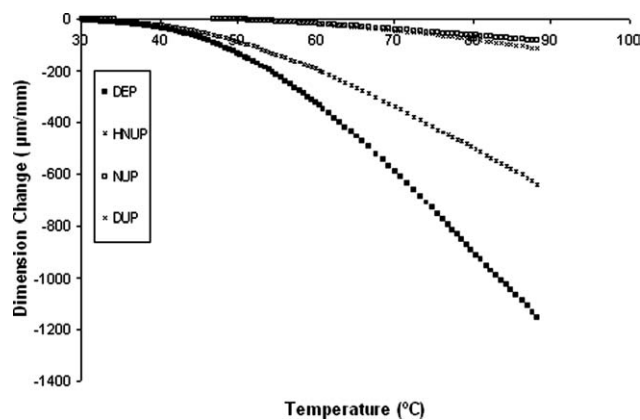

Figure 16 TMA curves of foams prepared with branched chained phthalate ester plasticizers.

poor quality with large and striking defects. Thus, uniform foams have a uniform density close to the nominal one, whereas poor foams have a nonuniform density showing large bubbles and denser parts with larger density than the nominal one. The color of the foam may be also indicative of the stretch the sample has undergone. Also the possible contractions experimented by the sample during the cooling may alter the final dimensions of the molded part. All these aspects, in addition to the possible failures, large bubbles significantly affect the density of the sample. Table II shows the density of the uniform part of the obtained foams, and this value has been used to normalize the TMA curves reported.

Figures 15 and 16 show the TMA curves of the plastisols, corrected with the corresponding foam density. It can be observed that the softest foams (i.e., the largest slopes of the corresponding graphs) are from the formulations prepared with DEP, DIBP, and HNUP. A correlation of these curves is observed with the molecular weight. Generally, the higher the molecular weight the higher the resistance of the sample, as expected.

Determination of the bubble size distribution

The bubble size distribution has been obtained as described in the experimental section. The average
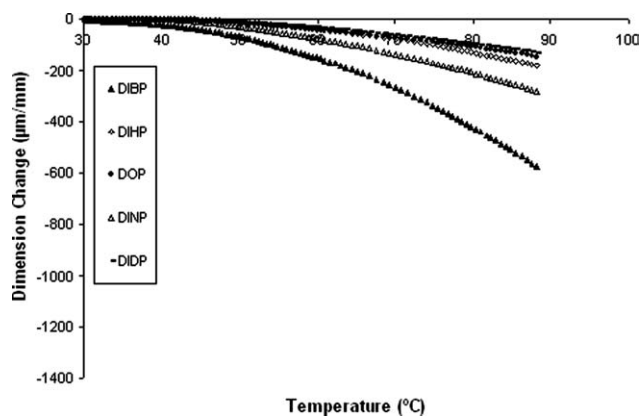
bubble size and the standard deviation are two parameters widely used to characterize the distributions. In Figures 17 and 18, photographs of the foams show their morphology, the plasticizer, average bubble size, and the standard deviation values. Tables III and IV show the average bubble size and the corresponding standard deviation (in mm) for the two groups of plasticizers: the linear and branched chained phthalates, respectively. Good-quality foam has a uniform aspect with a homogeneous bubble size distribution, mainly with small sizes and small standard deviation. According to all the results obtained, it can be observed that the best-quality foams are prepared with those phthalate ester plasticizers that have the smallest molecular weight, such as DEP, DIBP, and DIHP. On the contrary, foams prepared with higher molecular weight plasticizers have poor quality with larger average size and/or standard deviation, with a less homogeneous bubble size distribution. All these facts can be explained by the plasticizer compatibility with the PVC-VA resin particles.

To classify the foams, several comparisons were made according to the molecular weight of the plasticizer, foam aspect, color, average bubble size, and standard deviation. For the foams studied, there is a negative correlation between molecular weights and bubble size, whereas the correlation with standard
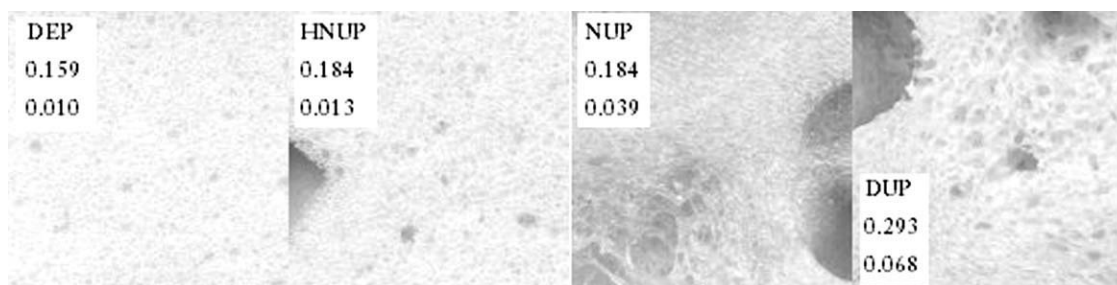

Figure 17 Photographs of foams prepared with linear chained phthalate ester plasticizers.
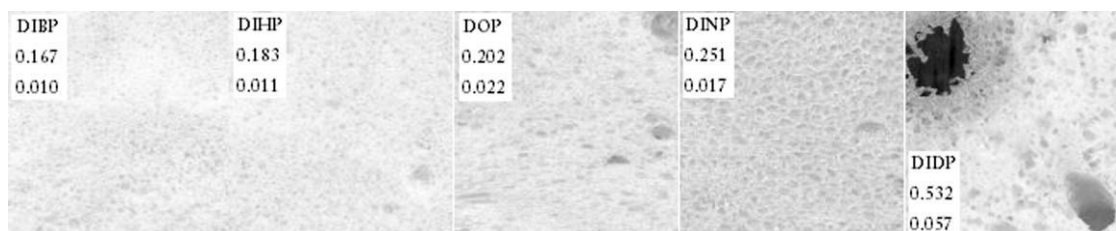
Figure 18 Photographs of foams prepared with branched chained phthalate ester plasticizers.

deviation is positive, resulting in a foam of poor quality, as shown in the Figures 17 and 18. All the foams seem to follow the same trend, which can be also observed from the average bubble size and standard deviation values respectively, presented on the thumbnails. The lower molecular weight results in earlier gelation and higher viscosities, earlier decomposition of the chemical blowing agent and narrower peaks, higher slope in extensional viscosities and TMA penetration, and more homogeneous bubble size distribution with a small average size and standard deviation.

In Figure 17, the morphology of the foams produced from linear phthalates can be compared. It can be emphasized that the foam prepared from DEP has the smallest average bubble size and deviation. HNUP and NUP have the same average size; however, their standard deviation values are different. The poorest quality developed by the foam was that prepared from DUP, which has the largest mean bubble size with the largest standard deviation. Foam quality seems to be strongly influenced by the molecular weight of the plasticizer used. TMA penetration resistance results also show that the highest slopes are presented by DEP and HNUP which means that these two foams are the most flexible and softest ones.

Figure 18 allows the difference to be observed between the foams of the branched chained phthalate ester plasticizer group. DIBP and DIHP have the best aspect (homogeneous distribution) with the smallest mean size and standard deviation. Compared with the TMA results, it can also be observed that these foams are the softest of this group. DOP is the most commonly used phthalate ester plasticizer

for flexible foam production. In this study, we have also considered its foam to be relatively uniform and of good quality; however, foams of DIBP, DEP, and DIHP are much better as the photos clearly show. DOP and DINP present similar quality foams, while DIDP has striking defects, large holes, and consequently higher mean size and less homogeneous distribution. This is a consequence of the lower compatibility of the DIDP plasticizer with the PVC-VA because of the longer chains and higher molecular weight of this plasticizer in addition to the early ADC decomposition that makes the matrix not able to withstand the pressures developed by the decomposition of the blowing agent.

CONCLUSIONS

From the results obtained the following conclusions can be obtained:

Plastisol gelation and fusion and thermal transitions of the paste and blowing agent decomposition process seem to be strongly influenced by the type, chemical structure, chain structure, compatibility, and molecular weight of the plasticizer.

Clear correlation of temperatures of maximum viscosity and their corresponding viscosity values with the molecular weight and chemical nature of the plastisols have been observed. The linear phthalates seem to be more compatible with the resin yielding higher maximum viscosities of the plastisols in the dynamic experiments than the corresponding branched phthalates of the same molecular weight. The analysis of the viscosities at two temperatures of the phthalate plasticizers has revealed very important features for understanding the eventual

TABLE III
Average Bubble Size and Standard Deviation-Linear Chained Phthalates

Plasticizer	Average bubble size (mm^2)	Standard deviation
DEP	0.159	0.010
HNUP	0.184	0.013
NUP	0.184	0.039
DUP	0.293	0.068

TABLE IV
Average Bubble Size and Standard Deviation-Branched Chained Phthalates

Plasticizer	Average bubble size (mm^2)	Standard deviation
DIBP	0.167	0.010
DIHP	0.183	0.011
DOP	0.202	0.022
DINP	0.251	0.017
DIDP	0.532	0.057

behavior of the corresponding plastisols during their processing.

Studying extensional viscosity of the pastes may provide complementary information to the complex viscosity for understanding the results of the foaming process.

A linear trend has been observed among the molecular weight of the plasticizer and the T_g of the PVC-VA resin in the corresponding plastisols with different commercial plasticizers. The linear phthalates seem to be more compatible with the resin yielding lower T_g than the corresponding branched phthalates of the same molecular weight. The chemical blowing agent decomposition temperature also follows a linear trend except for the DIDP.

Characterizing the final foam product, it can be emphasized that foams of relatively good quality are prepared with plasticizers of the smaller molecular weight, which are more compatible with the PVC-VA resin. These plastisols have earlier gelation with elevated viscosities, and fully developed properties at the temperatures of the ADC decomposition. On the contrary, formulations prepared with less compatible plasticizers have late gelation with lower viscosity and slower bubble formation, thus resulting in poorer quality foams.

Consequently, as a final conclusion it can be stated that the molecular weight of the plasticizer is of crucial importance in the foaming process as clear correlations observed and discussed in this study. The knowledge of the evolution of the complex viscosity with temperature and the kinetics of the blowing agent decomposition are the two factors mostly explaining the plastisol foaming process.

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