

Extensional Viscosity Measurements and Characterization of Poly (vinyl chloride-co-vinyl acetate) Plastisols and Foams

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ABSTRACT: The foaming of PVC-VA [Poly (vinyl chloride-co-vinyl acetate)] plastisols is a complex combination of processes involving the simultaneous curing of the paste with the evolution of gases caused by the decomposition of the chemical blowing agent. The extensional viscosity is a fundamental characteristic of the material, responsible for the behavior of the system when undergoing the extensional stress produced by the released gases. Nevertheless, such changes have not been considered to the same extent as the complex viscosity evolution or the thermal processes suffered by PVC-VA plastisols. The objective of the present work is to study the extensional viscosity of the PVC-VA plastisols prepared with three plasticizers of similar structure, but with different curing and rheological behavior in order to investigate its influence on the quality of the foams obtained. Extensional viscosity measurements under forced prestretch conditions revealed that depending on the structure and consequently on the compatibility of the plasticizer used, each plastisol develops its properties and structure accordingly. DINCH plasticizer (Diisononyl cyclohexane-1,2-dicarboxylate presenting alicyclic ring) seems to be the less compatible compared with the other two studied (both presenting aromatic rings) according to its behavior during the curing and foaming processes and may not be able to withstand the pressure evolved by the released gases during the foaming process yielding foams of poorer quality. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: poly (vinyl chloride-co-vinyl acetate); rheology; extensional viscosity; plasticizer; plastisol; foam

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INTRODUCTION

Over the last 30 years, foaming fundamentals and technology have experienced an enormous development.^{1–3} In foaming processes the polymer is subjected to a series of dynamic processes including the blowing agent dissolution or decomposition. Strikingly different processes are present in the manufacturing of foamed articles, with different effects (with both qualitative and quantitative consequences) on the processability and final properties developed. Obviously, the type of process depends on the polymer matrix and on the blowing agent (BA) used. Polymer matrices may be polymers already formed with their properties fully developed (e.g., PE, PP, PS, PVC), or curing or reactive systems as PVC plastisols,⁴ as one example representative of this group. The blowing agent can be solved gas⁵ (e.g., CO₂ or fluorocarbons) or chemical compounds⁶ decomposing during the process and evolving gases. Additives and fillers^{5,7} have additional effects on processing and properties. Thus, depending on the selected combination, the system may present very different behavior during the processing. Nevertheless, all foaming processes⁸ may have many similarities based on the evolution of

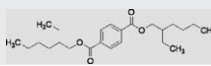
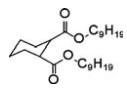
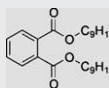
the rheological properties of the polymer matrix, their melt strength⁹ and drawability,¹⁰ as well as the solubility of the BA or its capability and kinetics of gas generation, the bubble nucleation and growth, and so on. These are of paramount importance in the understanding of the behavior of this dynamic system.

Unfortunately, rheological properties of polymers and polymer/BA mixtures are notoriously difficult to determine.⁸ Nevertheless, the different rheological properties of the polymer melts are the subject of an enormous amount of literature, and the efforts devoted to the different properties are innumerable. Hence, the shear viscosity of polymers and the effect of the additives and fillers, the temperature and pressure, the structure of the polymer and other properties are very well known for most of the polymer systems, including the PVC plastisols.

The extensional or elongational flow of polymer melts, which is extremely important due to the industrial relevance of this type of flow in most of the polymer transformation processes and foaming^{8,9} is not as extensively studied as the shear flow.

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Table I. Properties and Producers of the Plasticizers Studied

Plasticizer	Abbreviation	Commercial name	Chemical structure	Density (g/cm ³)	Molecular weight (g/mol)	Supplier
Bis(2-ethylhexyl)-1,4-benzenedicarboxylate	EHBDC	Eastman 168		0.984	391	Eastman
Diisononyl cyclohexane-1,2-dicarboxylate	DINCH	Hexamoll DINCH		0.949	425	BASF
Diisononyl Phthalate	DINP	Palatinal N		0.973	421	BASF

Another very important property of the matrix still less considered in literature, is the melt strength,^{11–13} which—according to Kozłowski⁹—can be measured by applying force to the extruded material stream, during stretching under uniaxial stress, up to the break of a material.

In a recent PhD thesis by Wang,⁸ a very clear description of the blowing processes is presented, and the effect of all the processes involved is discussed. This work is focused on polylactic acid/CO₂, which is a nonreactive matrix system with a physical BA. The knowledge of the basic rheological properties—as a function of the polymer structure—of the system was successfully used to modulate the properties of the foam obtained. However, these authors recognized the difficulty of the determination of these properties and the clear understanding of their relations and effects on the properties of the final product.

Regarding curing of reactive polymer systems, such as PVC plastisols,⁴ the subject of this work, many papers have been found dealing with the shear viscosity^{14–17} of the systems during curing and melt strength⁹ of plasticized PVC systems. However, we have found no papers dealing with such determinations on PVC (-VA) plastisols. These properties are even more important when the process selected is rotational molding^{18,19} to obtain foamed articles.

With regard to the foaming of a PVC plastisol with a chemical blowing agent (CBA, such as the azodicarbonamide: ADC), the problem is much more complicated than in the case of a non-reactive polymer, since the behavior of the polymer matrix changes in a different way. Thus, the shear viscosity, the extensional viscosity and melt strength are strongly influenced by such changes during the transformation process of the plastisol suspension to a fused homogeneous material. These changes are not present in a nonreactive system, and must be considered in addition to the other parameters. (i.e., effects of the additives, the possible interactions and the decomposition kinetics of the ADC, the solubility of the gases generated, and the eventual volatilization of the plasticizer during the process or the thermal degradation of PVC^{9,20,21}).

The determination of the extensional viscosity and melt strength of such structure-changing systems is also much more difficult than in the case of a conventional polymer. It is very well known^{14,22} that both the extensional viscosity and the melt strength of the plasticized PVC must be very different, than in that of a plastisol during the curing process. Such properties and

changes, fundamental for a better understanding of the system, have to be considered and monitored during the processing.

In previous works,^{23–26} we studied the effect of the nature of different plasticizers in the properties and morphology of the foams obtained from foamable PVC plastisols by rotational molding process. We studied the evolution of the complex viscosity during the curing process,²⁷ the extensional viscosities,^{25,26} the thermal effects during the swelling of the resin and the decomposition of the ADC,²⁸ as well as the morphology and characteristics of the foams obtained.^{25,26} Interesting relationships were obtained among all these properties and the foams obtained, showing that once cured, these systems behave in a similar way to other nonreactive systems. Nevertheless, at the practical ADC decomposition temperature the system, depending on the plasticizer used, may be still developing its structure and may behave in a rather unexpected way.

The objective of this work is to study the extensional viscosity of the plastisols prepared with three plasticizers of similar structure, but with different curing and rheological behavior. Different test conditions were applied in order to indirectly show the effect of the degree of development of the melt strength of the system on such properties. To reach this objective, the extensional viscosity of partly cured plastisol samples were measured in the ARES (TA Instruments) after being treated under different prestretch and extensional rates such as test conditions and temperatures. (Samples must be partly cured in order to enable the extensional viscosity measurements in the ARES rheometer).

EXPERIMENTAL

Materials

Resin. To prepare the plastisol formulations, ETINOX 400 PVC resin (E400—a vinyl chloride-vinyl acetate copolymer with a nominal 5% of vinyl acetate by AISCONDEL was used. Typical values provided by the supplier are 4.8% of comonomer and a *K* value of 70.

Plasticizers. Table I shows the plasticizers selected, the abbreviation, the commercial name, chemical structure, the density, and molecular weight as well as the producers.

Reagents. Table II shows the stabilizer, the costabilizer, the kicker, and the chemical blowing agent used along with the commercial name, the chemical components and the supplier.

Table II. Reagents Used

Reagent type	Commercial name	Composition	Producer
Stabilizer	CL 4	Ca / Zn stearate	REAGENS
Co-stabilizer	Lankroflex 2307	Epoxidized Soybean oil (ESBO)	AKCROS CHEMICALS
Catalyst (kicker)	Zinc oxide	Zinc oxide (ZnO)	PANKREAC
Foaming Agent	D 200 A	Azodicarbonamide (ADC)	UNICELL

METHODS

Plastisol Preparation

Three PVC plastisols were prepared by mixing 100 phr (parts per hundred resin) of ETINOX 400 PVC-VA resin from AISCONDEL, 100 phr of one of the 3 plasticizers, 2 phr of Reagens CL4 commercial Ca/Zn stearate stabilizer, 6 phr of Lankroflex 2307 epoxidized soybean oil 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.

Plastisol Characterization

Evolution of the Complex Viscosity in a Bohlin CS 50 Rheometer. Evolution of the complex viscosity of the plastisols was determined by measuring complex viscosity in dynamic oscillatory tests between 40 and 180°C at 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.

Evolution of the Extensional Viscosity in an ARES (Advanced Rheometer Expansion System). The extensional viscosity of $10 \times 18 \times 1$ mm³ samples (previously cured at 180°C for 10 min) was measured at 160, 170, and 180°C. At each temperature, samples were conditioned by prestretching them up to a 0.31 mm prestretch at three different prestretch rates (i.e., 0.1, 0.5, 1 s⁻¹). After a 50 s relaxation time the extensional viscosity measurements were carried out at five different extensional rates (i.e., 0.1, 1, 5, 10, 15 s⁻¹) using the Extensional Viscosity Fixture (EVF) Accessory.

Thermal Behavior and Decomposition of the Chemical Blowing Agent by Differential Scanning Calorimetry (DSC). Thermal transitions 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 cm³/min flow at 20°C.

Foam Production

Rotational Molding. Plastisols were poured into a cylindrical mold and placed into the Rotospeed RL 1-400 rotational molding machine. Two cycles were done: the first cycle (curing) occurs at 210°C for 8 min with a 10 : 2 rpm arm : wheel speed ratio, while the second cycle (cooling) involves 2 min airflow, 10 min water flow and finally 2 min airflow.

Foam Characterization

Determination of the Average Bubble Size and Standard Deviation. Photographs of the cross section of the foam parts prepared were taken and analyzed by using various imaging pro-

grammes (GIMP, Image J, Paint, Photoshop) and statistic steps. Reliable results were obtained for the average radius and the standard deviation of the corresponding distributions.

RESULTS AND DISCUSSION

Plastisol Characterization

Evolution of the Complex Viscosity. The changes occurring during the curing of a PVC plastisol are very complex and have been widely studied.^{27,29,30} The evolution of the complex viscosity under an increasing temperature profile is probably the most popular technique to monitor this type of processes.³¹ The viscosity of the paste starts to decrease, as the viscosity of the plasticizer decreases with increasing temperature in the initial PVC suspension. As the temperature increases, the interaction between the plasticizer and the polymer particles starts. This is the swelling^{32,33} of the PVC particles in the plasticizer. During the swelling the viscosity increases sharply. Such interactions continue at higher temperatures, and the PVC crystallites start to fuse together with the plasticizer, thus forming a homogeneous material.²² Here, another increase in the complex viscosity might occur and can be observable depending on different variables (such as the type of resin, the type and concentration of the plasticizer, additives, etc.) In the next stage, the system is fully develops its structure and its viscosity decreases with the temperature, as corresponds to a polymer solution. The knowledge of these behaviors is fundamental for the understanding of the processing of these materials, especially in rotational molding,¹⁸ where all these changes occur in the industrial process.

The three plasticizers considered have similarities in the structure and molecular weight (M_w), as can be seen in Table I. We have chosen Bis(2-ethylhexyl)-1,4-benzenedicarboxylate (EHBDC, M_w : 391) from Eastman, Diisononyl Phthalate (DINP, M_w : 421) and Diisononyl cyclohexane-1,2-dicarboxylate (DINCH, M_w : 425) from BASF to make a comparative study. EHBDC is a benzene ring substituted with two branched chained (i-octyl) carboxylate groups in the para (1,4) position. DINP presents similar structure having two branched chained (i-nonyl) carboxylate groups in the orto (1,2) position of the aromatic benzene core. DINCH presents the same chains in the same position as DINP; however, its chains are attached not to an aromatic benzene core, but to a cyclohexane core in chair conformation. Consequently, they occupy different space. The benzene derivatives (EHBDC and DINP) are planar and present aromaticity, while DINCH has a chair conformation because of the non-aromatic (alicyclic) cyclohexane ring. In previous papers,^{25–28} we studied 20 plasticizers of 8 different chemical families and found certain correlations between the molecular structure of the plasticizer used and the structural changes undergone by the corresponding plastisols, as well as the

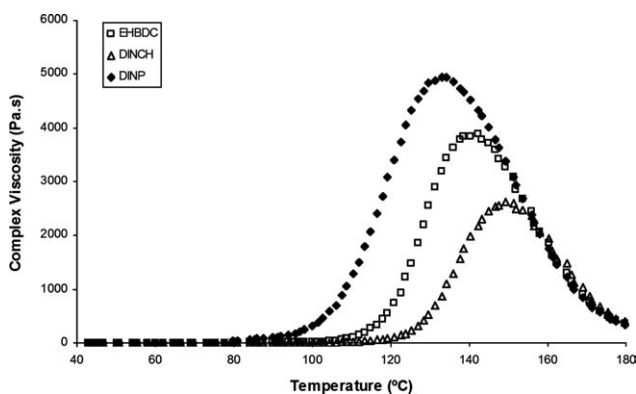


Figure 1. Evolution of the complex viscosity of plastisols prepared with EHBDC, DINCH and DINP plasticizers.

foaming and foam quality. Taking those results into consideration to discuss such correlations and provide a better insight into these changes and processes became interesting.

According to the literature^{25,34–36} several properties of the plasticizers and additives used can influence the plasticization of the PVC resin. These properties are, the molecular weight, the molecular volume, the polarity of the molecules and other structural parameters which determine the solvent power and the plasticizer compatibility with a PVC resin particles.³⁷

Phthalates in general have medium polarity,³⁵ and the other two dicarboxylate type plasticizers studied (DINCH and EHBDC) have similar structures and molecular weights to the DINP. EHBDC, which is a terephthalate, presents a very similar swelling temperature to that of the DINP, showing that the “para” position of the chains has very little influence on the compatibility, as we have shown in a previous publication where we studied the corresponding evolved heat in the DSC measurements. DINCH provides the highest swelling temperature, thus being the less compatible plasticizer, probably as a result of the lower polarity of the alicyclic structure as compared to the aromatic ring of the DINP and EHBDC. These findings are in good agreement with the gelation studies carried out with these plasticizers.^{25,27}

Howick³⁶ studied the molecular interactions between PVC and plasticizers, and in the plasticization mechanism. Several plasticization theories had been proposed in order to explain the plasticizer action, however the most important ones are the free volume and the lubricity theory.³⁸ According to the mentioned literature, the plasticizers which occupy the greatest volume are more compatible with the PVC resin, since they add maximum free volume to the resin. Thus the plasticization is more successful and therefore facilitated.

In Figure 1 the evolution of the complex viscosity of the studied plastisols can be observed.

As already discussed,²⁷ it seems that the phthalate ester type plasticizer DINP (M_w 421) which has an aromatic ring with chains of medium polarity is more compatible with the PVC resin used than the DINCH which has an alicyclic ring with similar chains and molecular weight. Plastisols prepared with DINP present earlier gelation with more elevated complex vis-

cosities than plastisols of DINCH with similar molecular weight, and EHBDC follows an intermediate behavior. Nevertheless, at temperatures above 160°C, the trend of the complex viscosity is inverted and the DINCH is the plasticizer showing the larger viscosity, whereas the DINP is the less viscous one.

Evolution of the Extensional Viscosity. The extensional viscosity of the polymers is a fundamental property explaining the behavior in foaming processes.^{8,39} Many papers deal with the measuring of this important property and its effect in the processing. In the case of PVC plastisols, the literature found is not very abundant and only few references^{40–42} have been found. Moreover, we have not found any reference dealing with the extensional viscosity in the processes of foaming of PVC-VA plastisols. In previous papers, we studied the effect of different plasticizers in such processes and we reported data on the extensional viscosity of the corresponding pastes at given temperatures.^{25,26} The effect of the extensional viscosity on the behavior of the system was not as clear as the effect of the complex viscosity or other properties of the system. In this article, we have selected three plasticizers in order to try to clarify the effect of the extensional viscosity of foaming process and the properties of the foams obtained.

Figures 2–4 show how the extensional viscosity develops in the case of the three studied plasticizers under the same measurement conditions (160°C with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹). In these cases, it can be seen that most of the curves follow similar trends, showing the shear thickening behavior typical of PVC plastisols.⁴³ However, DINCH presents larger values of the extensional viscosity than the other two plasticizers, (e.g., at 160°C P 0,1 s⁻¹ E 15 s⁻¹ at 0,1 s; EHBDC reaches 6774 Pa s, DINCH reaches 9376 Pa s, and DINP reaches 5851 Pa s) which is in good agreement with the complex viscosities observed at temperatures above 160°C. Thus, these DINCH plastisols should be able to withstand the pressure developed by the gases eventually released during the foaming process at this temperature range, if their melt strength is fully developed.

Nevertheless, it may be that not all samples have developed their final properties. It has to be considered moreover, that the ARES measurements were carried out on previously cured

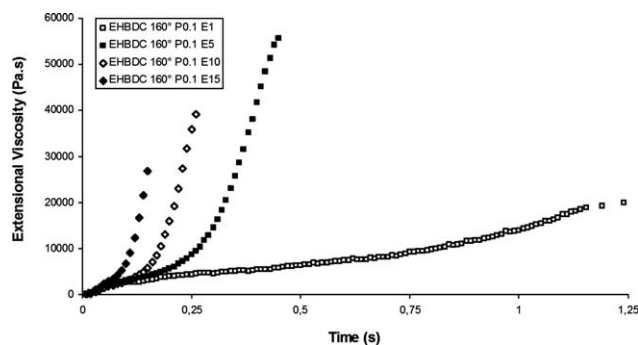


Figure 2. Extensional viscosity curves of samples prepared with EHBDC plasticizer at 160°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

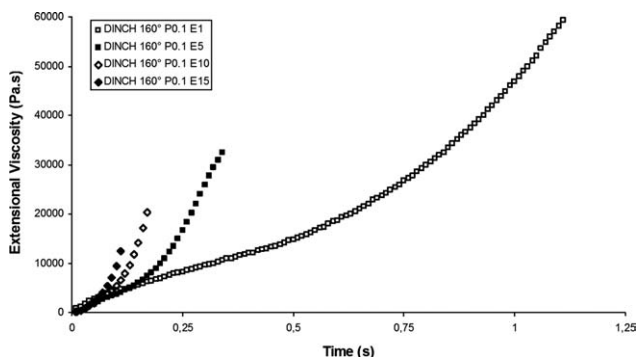


Figure 3. Extensional viscosity curves of samples prepared with DINCH plasticizer at 160°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

samples at 180°C for 10 min and such conditions may be not enough to ensure that all the samples, especially the slowest curing plastisols, have completely undergone all the curing transformation processes, and have consequently fully developed their final properties.

The extensional experiments at 160°C and a prestretch of 1 s⁻¹ clearly show that the curing conditions used are not enough in the case of the DINCH plastisol (the one showing the highest gelation temperature as shown in Figure 6). This sample is not capable of withstanding the stress imposed during the conditioning at such a high prestretch rate, and breaks during such treatment, thus proving that this plastisol has not fully cured and developed the required melt strength. Moreover, the pre-cured samples which have fully developed their new properties (i.e., those with DINP and EHBDC) can withstand the elongational stresses even under the forced or inconvenient measurement conditions, such as 160°C P1. Figures 5 and 7 show that under the same conditions, EHBDC and DINP samples behave normally, as expected for a fully cured plastisol.

Figures 8–10 show the extensional viscosity of the three plastisols at 170°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹, while Figures 11–13 show the corresponding data under the same conditions but with 1 s⁻¹ prestretch rate. It can be observed that all plastisols,

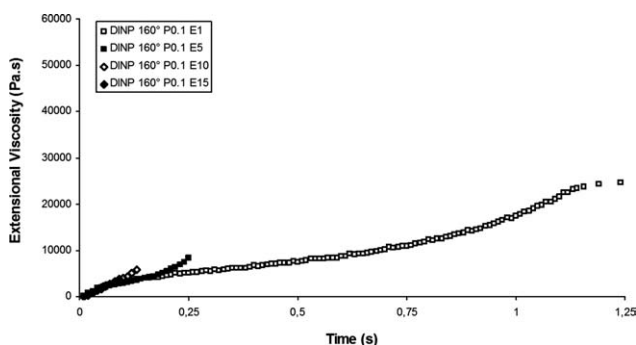


Figure 4. Extensional viscosity curves of samples prepared with DINP plasticizer at 160°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

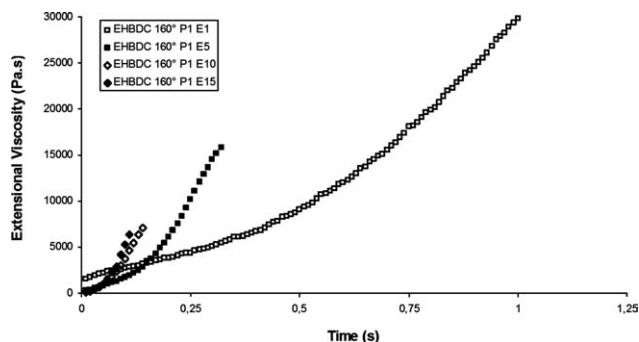


Figure 5. Extensional viscosity curves of samples prepared with EHBDC plasticizer at 160°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

including that prepared with DINCH, now behave in the expected way and all three can withstand both prestretch rates used, even the forced one (1 s⁻¹). In this case, it seems that the DINCH plastisol completes its structural changes during the extensional viscosity measurements at 170°C and has developed its final melt strength. On the other hand, the extensional viscosity measured at 170°C is lower than that obtained at 160°C.

Figure 13 shows a wide scatter of the data for the DINP plastisol at 170°C. This plasticizer is the most compatible one of the three tested. Sugimoto et al.⁶⁴ observed this type of behavior when studying the sol–gel transitions of suspension PVC plastisols with different amounts of DINP and 5 phr of CaCO₃. The samples with 45.5% of the resin started showing this type of scatter when measuring at 180°C, which was associated to the gel state of the plastisol which also loses its strain hardening behavior. It seems that this type of transition may occur for the present DINP plastisol at 170°C.

DSC and Thermal Transitions. It is important to consider the data, obtained from the DSC measurement along with the results of the complex viscosity measurements, for a better understanding of the foaming of a dynamic system such as the plastisols studied.^{25,26} The foaming has to be synchronized with the viscosity evolution as well, thus it is very convenient to study the relationship between the thermal transitions and the complex viscosity.

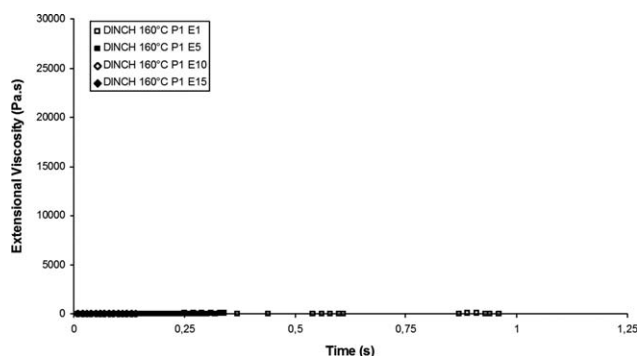


Figure 6. Extensional viscosity curves of samples prepared with DINCH plasticizer at 160°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

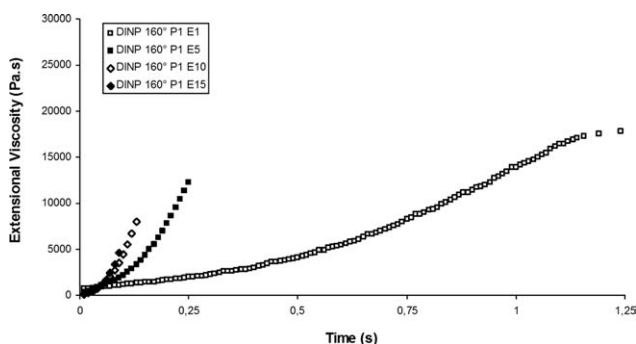


Figure 7. Extensional viscosity curves of samples prepared with DINP plasticizer at 160°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

During the DSC measurements two main processes can be observed resulting in two corresponding exothermic peaks. The first process is the swelling of the resin by the plasticizer. This process is obviously affected by the polarity and compatibility of the plasticizers. The less compatible plasticizer (i.e., DINCH) is the one which presents the highest temperature values for both processes.²⁸ The second peak corresponds to the decomposition of the chemical blowing agent used (gas generation). This process is also influenced by the plasticizer compatibility. In Table III the corresponding temperatures and heats are shown in each thermal process. It can be concluded that the less compatible plasticizer (which is in this case once again the DINCH) presents the highest temperatures for both processes when comparing it to the other two studied. Further important data should be considered, which is the difference between the decomposition temperature of the azodicarbonamide (T_{ADC}) and the temperature of the maximum complex viscosity (T_{η^*max}). This data provides relevant and useful information about the stage of development of the polymer matrix at the moment of the gas generation.²⁶ The larger this temperature difference, the more developed the properties and melt strength of the studied plastisol.

When a paste has still not fully developed its structure during the transformation processes, the sample would not withstand the pressure developed by the released gases during the foaming.

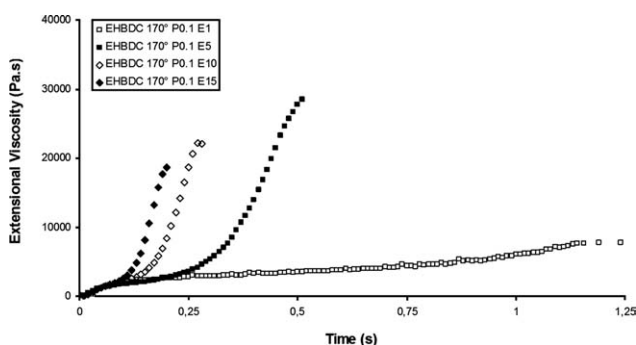


Figure 8. Extensional viscosity curves of samples prepared with EHBDC plasticizer at 170°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

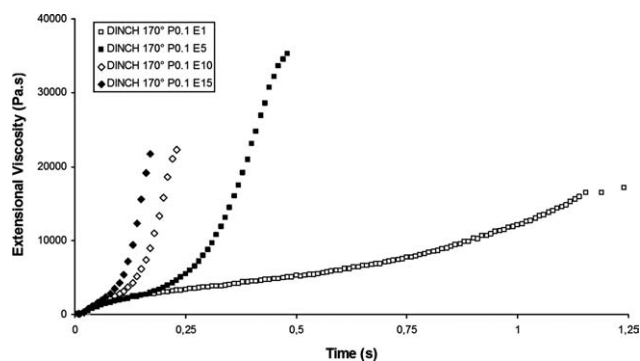


Figure 9. Extensional viscosity curves of samples prepared with DINCH plasticizer at 170°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

Consequently, a developed melt strength is necessary in the polymer matrix to withstand the stresses produced by the gas generated by the BA, and could therefore provide foams of good quality. According to the results presented in Table III, it can be deduced that the plastisol prepared with DINCH plasticizer has the narrower range in the temperature difference, which means that this plastisol has probably not developed the properties of a completely fused plastisol and cannot withstand the pressure evolved by the released gases either. This is again in good agreement with the fact (as will be shown in the next section) that the plastisol prepared with DINCH provides foams of poorer quality, showing several defects.

Plastisols of DINP present the largest temperature difference, which could be related to a better development of its final structure, which in turn results in the best quality foam of all three studied. EHBDC is found as intermediate between the other two, regarding both the temperature difference and the quality of the obtained foam. We have also shown elsewhere,²⁶ studying 11 plasticizers of 6 different chemical families, that this temperature difference is in a linear correlation with the compatibility and molecular weight of the plasticizer.

Foam Characterization

In this section of the article, we present the photographs of the obtained foams, and discuss the relationship between the

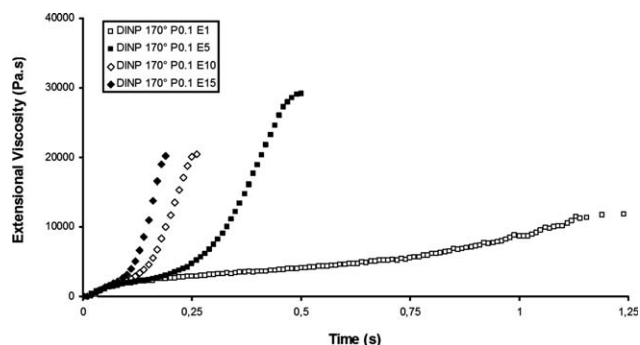


Figure 10. Extensional viscosity curves of samples prepared with DINP plasticizer at 170°C measuring temperature with 0.1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

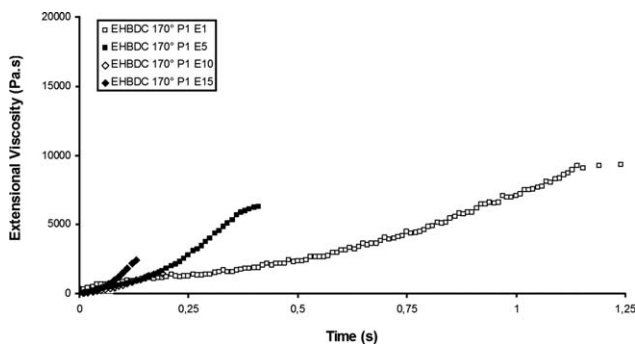


Figure 11. Extensional viscosity curves of samples prepared with EHBDC plasticizer at 170°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

plasticizer structure and the quality of the foam. In earlier publications, we provided a complete characterization of foams prepared with 20 different plasticizers,^{25,26} including these three studied.

Morphology of the Foams. Figures 14–16 show the morphology of the foams prepared with DINP, EHBDC, and DINCH obtained. Generally, all the foams present a long hole in the left side of the picture. This is because during the rotational molding process, a vent pipe was used to evacuate the gases evolved. Comparing the three foams studied, it can be observed that in the case of DINP plasticizer, the foam obtained has a very uniform aspect and covers the vent in a very even way. In the other two cases, the vent pipe acts as nucleating large bubbles and defects, and the general appearance of the foam is not as even as in the previous case. The foam prepared with DINCH shows the poorest quality with bigger bubbles, holes, and cracks.

Figure 14 shows the general aspect of the foam prepared with DINP plasticizer (*M_w*, 421). It can be clearly observed that this foam presents the most homogeneous aspect with similar cell sizes and the fewest defects comparing all the three foams. Although the vent pipe here also produces few defects, the foam has the best morphology. Excluding some tiny details—which can also be caused by a nonperfect mixing of the CBA—this foam is almost homogeneous.

Figure 15 shows the general aspect of the foam prepared with the EHBDC plasticizer. This foam presents a slightly worse ho-

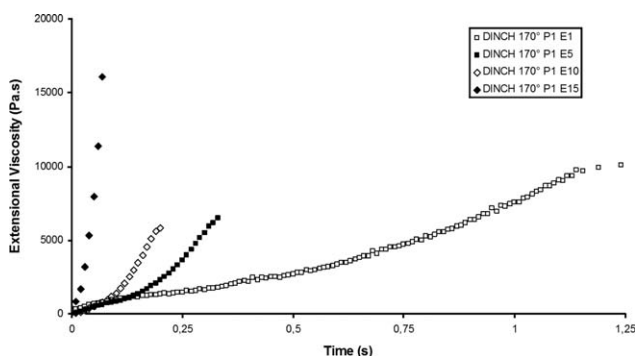


Figure 12. Extensional viscosity curves of samples prepared with DINCH plasticizer at 170°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

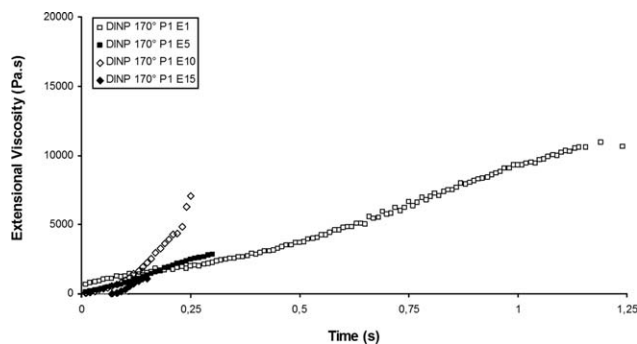


Figure 13. Extensional viscosity curves of samples prepared with DINP plasticizer at 170°C measuring temperature with 1 s⁻¹ prestretch rate and extensional rates of 1–15 s⁻¹.

mogeneity compared to the foam of DINP, as it has some larger bubbles and defects. The vent pipe here causes larger effects as well.

Figure 16 shows the foam prepared with the DINCH plasticizer. It can be clearly seen that the foam obtained with this plasticizer presents a poorer homogeneity than those corresponding to DINP and EHBDC. In the part of the vent, this plastisol presents very large defects and shows the coalescence of the large bubbles. The vent here generates a highly problematic area with different types of bubbles.

Taking into account its extensional and complex viscosity behavior along with its small temperature difference between the maximum complex viscosity and the CBA decomposition, it can be concluded that this plastisol has not fully developed its properties melt strength at the moment of the CBA decomposition. Thus, it is unable to withstand the stresses produced by the released gases. Furthermore, this foam has other defects such as several big bubbles and cracks in other zones too. This behavior must be related to the structure of this plasticizer, which presents an alicyclic ring, and therefore seems not to be as compatible with the PVC resin used as the other 2 studied.

Average Bubble Size and Standard Deviation of the Problematic Foam Parts-Presenting Defects.

In order to obtain a quantitative estimation of the average bubble size and its standard deviation, we have analyzed the right side of each specimen, which can be considered as representative of the foam obtained not or hardly affected by the vent pipe, but taking into account the large defects observed. In previous studies,^{25,26} we presented different results, since in that case we focused on the most

Table III. Results Corresponding to the Thermal Transitions of the Three Plastisols Studied

Plasticizer	First peak temperature (°C)	First peak heat (J/g)	Second peak temperature (°C)	Second peak heat (J/g)	T _{ADC} - T _{η[*]max} (°C)
EHBDC	72,0	0,18	175,4	11,49	33
DINCH	75,2	0,32	176,2	11,96	27
DINP	71,8	0,52	174,8	10,84	42

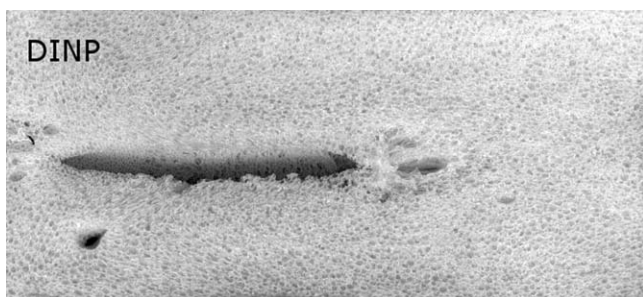


Figure 14. Photograph of the cross section of the entire foam obtained with the DINP plasticizer.

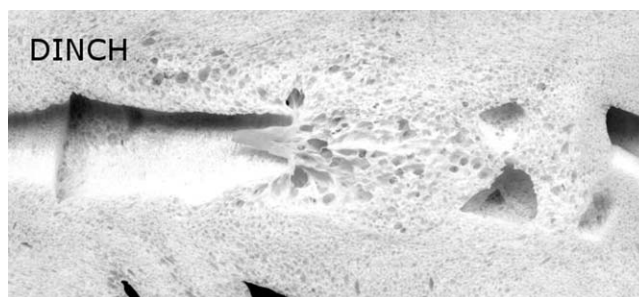


Figure 16. Photograph of the cross section of the entire foam obtained with the DINCH plasticizer.

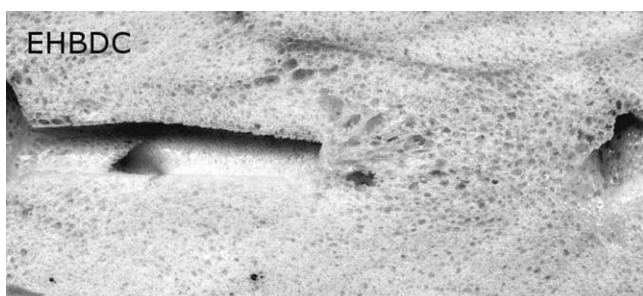


Figure 15. Photograph of the cross section of the entire foam obtained with the EHBDC plasticizer.

homogeneous parts of the foams obtained discounting the very large defects.

Figure 17 shows the parts of the foams selected for the analysis, including the corresponding average cell size and standard deviations (both in mm^2). Thus, the three foams studied can be easily compared. After this determination, it is obvious, that the best foam is provided by the DINP plasticizer, as the most homogeneous one, providing the smallest standard deviation and a very low average cell size. The EHBDC seems to be very similar, and DINCH provides strikingly different foam morphology and statistics. The conclusions made here, obviously agree with the previous ones obtained by the general observation of the foams in Figures 14–16.

A further correlation can be deduced between the extensional viscosity and the foam quality. That is, the plastisols prepared

with the DINCH plasticizer under some extreme conditions could not withstand the prestretch rate and they broke during the measurement. Extensional viscosity studies assist the understanding of the foaming behavior. The precured sample was broken because it had not yet developed its new structure and properties, until the moment of the gas generation, but finished its gelation process during the ARES measurement. Therefore this plastisol prepared with DINCH provides the poorest quality foams. Comparing the three plastisols and their corresponding evolution of the extensional viscosity, it has been observed that plastisols of DINCH reached somewhat higher viscosities at the same moment of the experiment, as the other two studied. Generally, the higher extensional viscosity should lead to better quality foams, however only in the case when the plastisol has already finished the processing and developed its properties. Since this did not happen in the case of DINCH, the best quality foam is provided by another plastisol formulation which has high enough extensional viscosity at the moment of the gas generation and also developed the required melt strength to be able to withstand the stresses during foaming. Nevertheless, DINCH could also provide foams of better quality if the CBA decomposition was delayed to occur when its melt strength was fully developed. This could be accomplished, for instance, by adjusting the amount of the ZnO catalyst.

CONCLUSIONS

- The DINCH alicyclic ring seems to be less compatible with the PVC resin used, than the aromatic ring of the orthophthalate (DINP) or terephthalate (EHBDC) plasticizers.

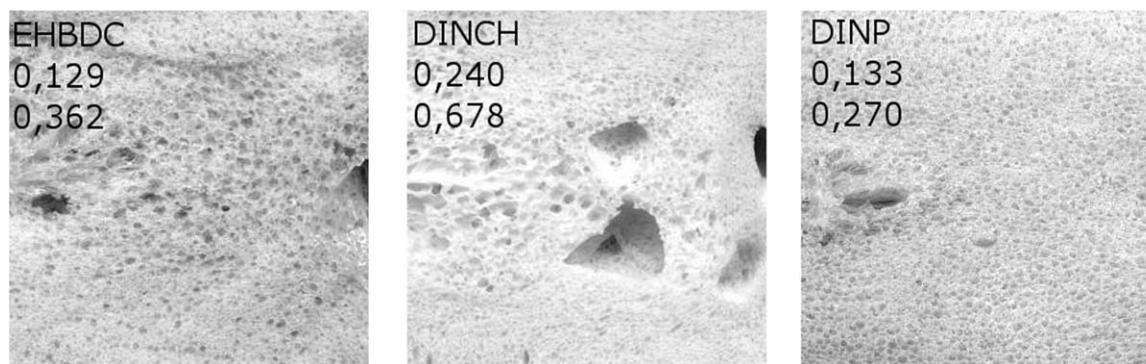


Figure 17. Photographs of the problematic parts of the foams obtained with EHBDC, DINCH, and DINP plasticizers.

- Extensional viscosity measurements under forced prestretch conditions have shown that the less compatible DINCH plasticizer is not as able to develop its properties under the same conditions as the other two studied, and that the plastisol prepared with DINCH may not be able to withstand the pressure evolved by the released gases during the foaming process, and thus presents a poor quality foam comparing to the others. However with a proper selection of the proportion of the kicker of the formulation, the CBA decomposition process could be delayed accordingly to allow this plastisol to develop the required melt strength and consequently lead to foams of good quality.
- The difference between the decomposition temperature of the azodicarbonamide (T_{ADC}) and the temperature of the maximum complex viscosity (T_{η^*max}) provides relevant information about the plastisol development. DINCH has the shorter temperature range, showing once again that the structural changes in this plastisol are not fully developed at the moment of the gas generation.
- The extensional viscosity is a very important property of the PVC plastisols to understand their foaming processes. High extensional viscosity favors the formation of foams of homogeneous bubble size distribution, if the plastisol has already developed all the required properties as well, at the moment of the gas generation.

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