# Soft PVC Foams: Study of the Gelation, Fusion, and Foaming Processes. II. Adipate, Citrate and Other Types of Plasticizers

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**ABSTRACT:** Plasticized poly(vinyl chloride) (PVC) is one of the most useful polymeric materials on an industrial scale because of its processability, wide range of obtainable properties, and low cost. PVC plastisols are used in the production of flexible PVC foams. Phthalates are the most used plasticizers for PVC, and in a previous article (part I of this series), we discussed the influence of phthalate ester type plasticizers on the foaming process and on the quality of the foams obtained from the corresponding plastisols. Because the use of phthalate plasticizers has been questioned because of possible health implications, the objective of this work was to undertake a similar study with 11 commercial alternative plasticizers to phthalates. The evolution of the dynamic and extensional viscosity and the interactions and thermal transitions undergone by the plastisols during the heating process were studied. Foams were obtained by rotational molding and were characterized by the determination of their thermomechanical properties, density, and cell size distribution. Correlations were obtained between the molecular weight and structure of the plasticizer and the behavior of the corresponding plastisols. After the characterization of the final foamed product, we concluded that foams of relatively good quality could be prepared with alternative plasticizers for replacing phthalates. Several plasticizers {Mesamoll (alkylsulfonic phenyl ester), Eastman 168 [bis(2-ethylhexyl)-1,4-benzenedicarboxylate], Hexamoll [di(iso-nonyl) cyclohexane-1,2-dicarboxylate], Citroflex A4 acetyl tributyl citrate (ATBC), and Plastomoll (dihexyl adipate)} were found to be interesting alternatives in the production of soft PVC foams because they provided very good quality foams with properties similar to, or even better than, those obtained with phthalate plasticizers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2981–2991, 2011

**Key words:** differential scanning calorimetry (DSC); molding; poly(vinyl chloride) (PVC); viscoelastic properties

## INTRODUCTION

In recent years, the use of foamed plastics has been increasing in all kinds of different applications because they can be manufactured from many different types of polymers, and their properties can be customized by the addition of additives[1,2] to specific requirements. Their outstanding properties, such as light weight, low density, excellent strength/weight ratio, superior insulating ability, and energy absorption capabilities, make polymer foams especially attractive in areas such as packaging, biomedicine, building, automotive, carpet underlays, textiles, furniture, and the production of toys.

In a previous work,[3] an extensive review of the scientific literature on polymeric foams,[4] their application,[5] and production[6] and the types and description of foaming processes[7] was provided. Furthermore, a deep introduction to plastisol rheology (gelation and fusion[8,9] processes, swelling,[10] and extensional viscosity[11,12]), calorimetric behavior of the plastisol,[13] and foaming agents[14] and a comprehensive exposition of the correlations found between all of these processes and their importance in the foaming process and foam quality was given. In that study, the rheological and thermal behaviors of the plastisols prepared with nine phthalate ester type plasticizers and the corresponding foam quality were studied. Phthalates are the most used plasticizers in flexible foam production; however, their application has been questioned lately because of possible environmental and health[15,16] implications. A further related issue is the migration[17,18] of these plasticizers, which is very important to be considered. For these reasons, the study of alternative plasticizers is convenient and highly recommended to find less questioned substitutes to produce the same or even better quality foams. Persico et al.[19] compared the behavior between dietylhexyl phthalate (DOP) and alternatives, such as dietylhexyl adipate (DOA) and acetyl tributyl citrate (ATBC). Furthermore, a short review of the application and properties of some alternative plasticizers has been found in the literature, dealing with different types of plasticizers,[20]

such as trimellitates, alkyl sulfonates [e.g., Mesamoll alkylsulfonic phenyl ester (ASE), benzoates (e.g., Benzoflex 2088), citrates (e.g., Citrofoll BII, known as ATBC)], and carboxylates [e.g., Hexamoll di(iso-nonyl) cyclohexane-1,2-dicarboxylate (DINCH)].

A very interesting review of the state of the art concerning the health issues of plasticizers can be found in the work of Wypich,[21] where three chapters are devoted to the health and safety issues of plasticizers and their environmental fate and regulations. However, not all plasticizers have been studied in a similar extension, and the availability of data is not the same, depending on the specific compound. Thus, whereas plasticizers such as DOP or DINP (phthalates in general) have been extensively studied for years from all the considered points of view, very few data have been obtained for other plasticizers.

To replace phthalates, a comparison should be made with other commercially available plasticizers with regard to their process performance and potential health issues. Other studies[22] have shown, for example, that DINCH possesses no environmental or reproductive hazards, and citrates have been approved for use in applications such as pharmaceutical tablet coatings, medical devices, and food packaging. Furthermore, it has also been emphasized and reported that all non-phthalate plasticizers are safe to use.

Thus, we chose 11 commercially available plasticizers of different chemical families to cover a wide range of properties (including two low-migration polymeric plasticizers), which have not been questioned from the point of view of health or environmental risks, to carry out a study of their suitability for foam applications, in a similar way as we did in the previous study with nine phthalate plasticizers.[3]

In other previous works, we studied the rheological[23] and thermal[13] behavior of 20 plasticizers of different families, such as linear and branched chained phthalates, monomeric and polymeric adipates, citrates, pentaerythrytols, carboxylates, and an alkyl sulfonate.

In the production of foams, several techniques can be used, such as extrusion or rotational molding.[24] The foaming process generally occurs at elevated temperatures at about 180–200°C and involves the curing of the plastisol (gelation and fusion) and the decomposition of the chemical blowing agent; this generates gases and then bubbles. To obtain good quality foams, all of these dynamic processes have to be adequately synchronized with each other. The development of the melt strength,[12,25] a property that indicates a compound's ability to withstand drawing without breaking, also plays a significant role in the foaming because the polymer matrix has to withstand the stresses evolved during the gas generation and bubble growth and stabilizes the foam structure. A high melt strength is fundamental for the production of foamed plastics with low density and good cell structure.

All of these parameters are influenced by the plasticizer type, structure, molecular weight (i.e., the compatibility with the resin), and the addition of other additives. For this reason, a proper selection of the adequate plasticizer and additives for the plastisol formulations is of crucial importance to obtain the required balance of properties in the final product.

The main objective of this work was to study the relationship among the evolution of the complex and extensional viscosities of the plastisols and the thermal processes occurring during their heating with the properties and quality of the foams obtained in the foaming process of such plastisols prepared with 11 commercial plasticizers of different chemical family alternatives to phthalates.

## EXPERIMENTAL

### Materials

#### Resin

The poly(vinyl chloride) (PVC) resin ETINOX 400 (a vinyl chloride–vinyl acetate copolymer with a nominal 5% of vinyl acetate; typical values provided by the supplier were 4.8% of comonomer and a K value of 70; where K is an indirect measure of the molecular weight of PVC, based on the viscosity of a PVC solution, and it is generally determined according to the standard test method DIN 53726) by AIS-CONDEL (Barcelona, Spain) was used to prepare these plastisol formulations.

#### Plasticizers

In the previous study,[3] 9 different commercial phthalate ester plasticizers were studied. In this study, 11 different commercial plasticizers from six different families were chosen. Among them were

- Two monomeric adipates [diisonoyl adipate (DINA) and dihexyl adipate (DHA)].
- Two polymeric adipates (PM 632 and PM 652).
- Two citrates [ATBC and acetyl trihexyl citrate (ATHC)].
- Two pentaerythrytol esters of fatty acids (H 600 and H707).
- Two carboxylates [DINCH and bis(2-ethyl-hexyl)-1,4-benzenedicarboxylate (EHBDC)].
- One ASE.

Table I shows the plasticizers selected, their abbreviations, their commercial names, their densities, their molecular weight, and their producers.

#### Reagents

Table II shows the stabilizers, costabilizers, kickers, and chemical blowing agents used, along with the

**TABLE I**
**Properties and Producers of the Plasticizers Studied**

| Plasticizer | Abbreviation | Commercial name | Density $(g/cm^3)$ | Molecular weight $(g/mol)$ | Producer |
|---|---|---|---|---|---|
| Monomeric adipates | | | | | |
| Dihexyl adipate | DHA | Plastomoll DHA | 0.935 | 314 | BASF, Barcelona, Spain |
| Diisonoyl adipate | DINA | Plastomoll DNA | 0.922 | 398 | BASF, Barcelona, Spain |
| Polymeric adipates | | | | | |
| Polymeric esters of adipatic acid | PM 652 | Palamoll 652 | 1.050 | 3300 | BASF, Barcelona, Spain |
| Polymeric esters of adipatic acid | PM 632 | Palamoll 632 | 1.145 | 7000 | BASF, Barcelona, Spain |
| Citrates | | | | | |
| Acetyl tributyl citrate | ATBC | Citroflex A4 | 1.050 | 402 | Morflex, Bracelona, Spain |
| Acetyl trihexyl citrate | ATHC | Citroflex A6 | 1.050 | 486 | Morflex, Barcelona, Spain |
| Pentaerythrytol esters | | | | | |
| Pentaerythrytol esters of fatty acids | H 600 | Hercoflex 600 | 1.000 | 604 | Hércules, Tarragona, Spain |
| Pentaerythrytol esters of fatty acids | H 707 | Hercoflex 707 | 1.000 | 750 | Hércules, Tarragona, Spain |
| Carboxylates | | | | | |
| Bis(2-ethylhexyl)-1,4-benzenedicarboxylate | EHBDC | Eastman TM 168 | 0.984 | 391 | Eastman, San Roque, Spain |
| Di(isononyl) cyclohexane-1,2-dicarboxylate | DINCH | Hexamoll DINCH | 0.949 | 425 | BASF, Barcelona, Spain |
| Alkylsulfonic phenyl ester | ASE | | | | |
| Mixture of ASE | ASE | Mesamoll ASE | 1.055 | 368 | Bayer, Barcelona, Spain |

commercial names, chemical components, and suppliers.

## Methods[3]

### Plastisol preparation

Eleven PVC plastisols were prepared by the mixture of 100 phr (parts per hundred resin) of ETINOX 400, 100 phr of 1 of the 11 plasticizers, 2 phr of Reagens CL4 commercial Zn/Ca–stearate stabilizer, 6 phr of Lankroflex 2307 epoxidized soybean oil as a 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 ($\eta^*$) and the extensional viscosity measurements]. For differential scanning calorimetry (DSC) measurements, foam production, and foam characterization, 2 phr chemical blowing agent [azodicarbonamide (ADC)] was also added to the same plastisol formulations.

### Plastisol characterization

*Evolution of $\eta^*$ by a Bohlin CS 50 rheometer (Malvern, United Kingdom).* Evolution of $\eta^*$ of the plastisols was determined by measurement of $\eta^*$ in dynamic oscillatory tests between 40 and 180°C at a 5°C/min heating rate with 20-mm-diameter parallel plates with a gap of 0.5 mm, an oscillation frequency of 1 Hz, and a controlled deformation of $5 \times 10^{-3}$ in a Bohlin CS 50 rheometer.
*Evolution of the extensional viscosity by an advanced rheometer expansion system (TA Instruments, Barcelona, Spain).* The extensional viscosities of the $10 \times 18 \times 1$ $mm^3$ samples, previously cured at 180°C for 10 min, were measured at 160, 170, and 180°C, with the application of a $0.1\text{-}s^{-1}$ prestretch rate and $5\text{-}s^{-1}$ extensional rate with the extensional viscosity fixture accessory at each temperature.

### Thermal behavior and decomposition of the chemical blowing agent by DSC

Thermal transitions, including the decomposition of the chemical blowing agent, was studied in a Perkin Elmer Pyris 6 DSC instrument (Rodgau, Germany) between 40 and 220°C at a 5°C/min heating rate in a nitrogen atmosphere with a 20 $cm^3$/min flow at 20°C.

### Foam production

*Rotational molding.* The plastisols were poured into a cylindrical mold and placed into a Rotospeed RL 1-400 rotational molding machine, Ferry Industries INC, Ohio, USA. Two cycles were made: the first cycle (curing) occurred at 210°C for 8 min with a 10:2 rpm arm-to-wheel speed ratio, whereas the

**TABLE II**
**Reagents Used**

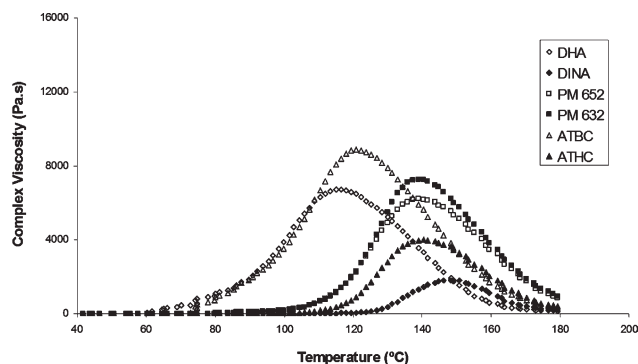| Reagent type | Commercial name | Composition | Producer |
|---|---|---|---|
| Stabilizer | CL 4 | Ca/Zn stearate | Reagens |
| Costabilizer | Lankroflex 2307 | Epoxidized soybean oil | Akcros Chemicals, Barcelona, Spain |
| Catalyst (kicker) | Zinc oxide | Zinc oxide | Pankreac, Barcelona, Spain |
| Foaming agent | D 200 A | ADC | Unicell |

**Figure 1** Evolution of $\eta^*$ (Pa s) of the adipate and citrate plasticizers.

second cycle (cooling) involved a 2-min airflow, a 10-min water flow, and finally, a 2-min airflow.

### Foam characterization

*Determination of the foam density.* A Mettler-Toledo Density Kit (Barcelona, Spain) for Analytical Balances was used. Appropriate sampling was 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 thermomechanical properties by thermomechanical analysis (TMA).* The penetration resistance of the foam was determined with a Setaram 92-16.18 TMA instrument (Caluire, France). Two heating cycles were applied: the first heating cycle was between 30 and 100°C at a 5°C/min heating rate in a nitrogen atmosphere without the application of force, and the second heating cycle was between 30 and 100°C at a 5°C/min heating rate in a nitrogen atmosphere with a 0.04-N force applied.

*Determination of the average bubble size and standard deviation.* Photographs of the cross sections of the foam parts prepared were taken and analyzed with various imaging programs (GIMP, Image J, Paint, and Photoshop) and statistical steps. Reliable results were obtained for the average radius and the standard deviation of the corresponding distributions.

## RESULTS AND DISCUSSION

This section is organized in the same way as in the previous publication;[3] that is, it is divided into two parts, that is, plastisol characterization and foam characterization. In the first part, the rheological and thermal behaviors of the plastisol formulations are considered, whereas in the second part, the foam characterization is discussed.

### Plastisol characterization

#### Evolution of the $\eta^*$

The results obtained for the temperature dependence of the $\eta^*$ of the 11 plasticizers selected are shown in

Figures 1 and 2. Figure 1 represents the curves for the plastisol formulations prepared with the two monomeric adipates (DHA and DINA), the two polymeric adipates (PM 632 and PM 652), and the two citrates (ATBC and ATHC) plasticizers, whereas Figure 2 shows the corresponding curves of the plastisols prepared with the two pentaerythrytols (H 600 and H 707), the two carboxylates (EHBDC and DINCH), and an ASE plasticizer. It can be observed that the gelation process of the formulations prepared with DHA, ATBC, and ASE occurred at low temperatures (>30°C lower than those of the other plasticizers) and developed higher viscosities than the rest of those studied. This fact may have been, on the one hand, a consequence of the higher compatibility of these plasticizers, which interacted in a more effective way with the PVC resin at this temperature range. On the other hand, it could have also been a consequence of possible plasticizer evaporation. The DHA, ATBC, and ASE plasticizers, which had the lowest boiling point values (i.e., 136, 171, and 200°C, respectively), were the more likely to evaporate under the process conditions. This fact may have resulted in a final product having a lower amount of plasticizer than the nominal one (i.e., that corresponding to the initial composition), which in turn, may have also resulted in higher developed viscosities; this was in good agreement with the literature with regard to the viscosity as a function of the plasticizer concentration.[26–28]

In a previous work,[23] we observed that the adipate-type plasticizers presented higher maximum viscosity temperatures, whereas the citrates developed lower maximum viscosity temperatures than the phthalates for a given molecular weight. Additionally, the adipates developed lower maximum viscosities than the citrates; in other words, the adipates seemed to be less compatible than the phthalates, and the phthalates were even less compatible than the citrates. These results were in good agreement with results reported by Persico et al.,[19] who studied ATBC, DOA, and DOP plasticizers. It was
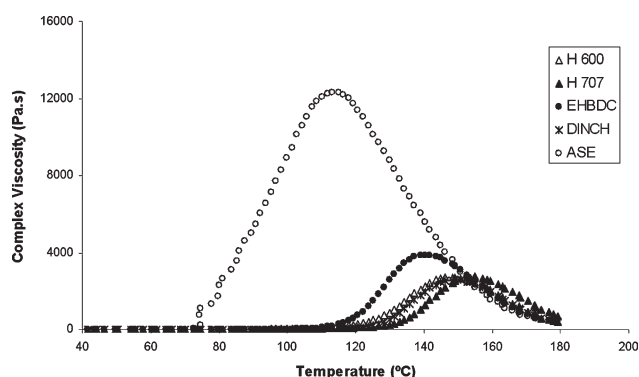


**Figure 2** Evolution of $\eta^*$ (Pa s) of pentaerythrytol, carboxylate, and the alkyl sulfonate plasticizers.

**TABLE III**
**Summary of the Results of the Evolution of $\eta^*$ and $T_{ADC}$**

| Plasticizer | $\eta^*_{max}$ (Pa s) | $T_{\eta^*max}$ (°C) | $\eta^*$ (Pa s) at 140°C | $\eta^*$ (Pa s) at 150°C | $\eta^*$ (Pa s) at 160°C | $\eta^*$ (Pa s) at 170°C | $\eta^*$ (Pa s) at 180°C | $\eta^*$ (Pa s) at $T_{ADC}$ | $T_{ADC}$ (°C) | $T_{ADC} - T_{\eta^*max}$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| Monomeric adipates | | | | | | | | | | |
| DHA | 6,740 | 116 | 3,320 | 1,620 | 584 | 232 | 154 | 246 | 170 | 54 |
| DINA | 1,820 | 149 | 1,460 | 1,800 | 1,110 | 423 | 219 | 326 | 173 | 24 |
| Polymeric adipates | | | | | | | | | | |
| PM 652 | 6,230 | 138 | 6,170 | 5,200 | 3,480 | 1,750 | 842 | 2,254 | 167 | 29 |
| PM 632 | 7,290 | 138 | 7,260 | 5,880 | 3,750 | 1,900 | 950 | 3,517 | 161 | 23 |
| Citrates | | | | | | | | | | |
| ATBC | 8,900 | 121 | 5,620 | 3,430 | 1,730 | 783 | 396 | 941 | 167 | 46 |
| ATHC | 3,990 | 140 | 3,990 | 3,370 | 2,010 | 842 | 401 | 403 | 173 | 33 |
| Pentaerythrytol esters | | | | | | | | | | |
| H 600 | 2,730 | 148 | 2,260 | 2,680 | 2,000 | 979 | 418 | 930 | 170 | 22 |
| H 707 | 2,750 | 154 | 1,240 | 2,690 | 2,540 | 1,470 | 676 | 1,322 | 172 | 18 |
| Carboxylates | | | | | | | | | | |
| EHBDC | 3,880 | 142 | 3,850 | 3,180 | 1,850 | 841 | 366 | 503 | 175 | 33 |
| DINCH | 2,630 | 149 | 1,980 | 2,605 | 1,900 | 876 | 409 | 510 | 176 | 27 |
| ASE | | | | | | | | | | |
| ASE | 12,400 | 114 | 5,610 | 3,160 | 1,550 | 701 | 372 | 508 | 175 | 61 |

concluded that the tetrahedral conformation of the ATBC and the presence of four polar groups caused a fast incorporation of this plasticizer into the resin. In the case of DOA, the aliphatic linear structure did not seem to compensate for the lack of significant polarity and resulted in the slowest gelation plasticizer among them. The intermediate polarity of DOP seemed to justify its intermediate gelation temperature. In this study, the two carboxylate type plasticizers studied (DINCH and EHBDC) behaved similarly to the adipates (they had only two polar groups, whereas ASE presented similar compatibility to the citrates).

In previous studies,[3,23] when the rheology of the phthalate ester type plasticizers was examined, the data obtained was analyzed accordingly with the molecular weight of the plasticizer used. It was found that at elevated temperatures, after the maximum of each gelation curve, the plastisol $\eta^*$ tended to become lower when lower molecular weight plasticizers were used. Studying the developed viscosities at several temperatures between 140 and 180°C, we obtained interesting conclusions regarding the plastisol evolution, which led to a reliable interpretation of the results and also to a better understanding of the development of the final properties of each plastisol. It was found that at 140°C, not all of the plastisols had developed their final structure and properties. Only the most compatible (i.e., lower molecular weight) ones were capable of developing the final structure at 140°C, whereas at higher temperatures, all of the plasticizers had completed their structural changes to a larger extent. Each formulation, depending on the structure and molecular weight of the plasticizer used, may have been in a different stage of development of its properties and

new structure. Furthermore, the developed $\eta^*$ became a linear function of the molecular weight of the plasticizer in the case of the phthalate esters when their properties were fully developed. The deep knowledge of these processes is important for understanding the foaming behavior of such plastisols. In this case, the study of the 11 plasticizers of six different families made the comparison more complicated within each group, as only two plastisol formulations from each group could be considered. However, they also followed the same behavior within the corresponding family.[23] For this reason, we applied the conclusions of the previous publication for better interpretation of the results.

One of the main objectives of this study was to analyze the plasticizer effect on the foam quality. Thus, the analysis of the $\eta^*$'s at the processing temperatures and also at the decomposition temperatures of the chemical blowing agent (i.e., at the maximum decomposition rate) was convenient for discussing the dynamic behavior and eventual foaming processes of such pastes.

For these reasons, further data was considered to be important, which included the difference between the decomposition temperature of the azodicarbonamide ($T_{ADC}$) and the temperature of the maximum complex viscosity ($T_{\eta^*max}$). This temperature difference provided information about how the plastisol developed its viscosity, structural changes, and properties during the processing. Thus, both the $T_{ADC}$ and $T_{ADC} - T_{\eta^*max}$ values are presented in Table III. The wider this temperature range was, the more developed the properties and melt strength[12,25] of the plastisol formulations should have been; this is of crucial importance in the understanding of the dynamic foaming system. A developed melt strength
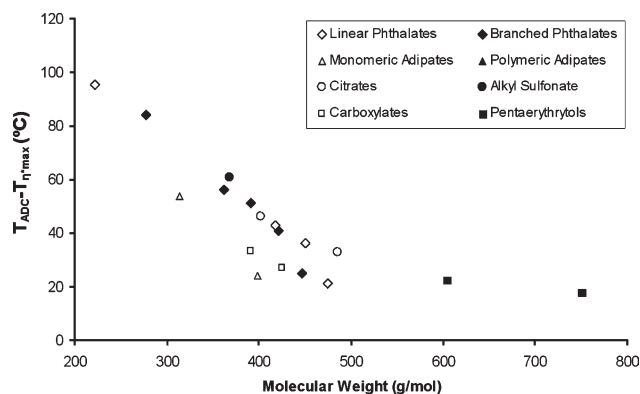
**Figure 3** $T_{ADC} - T_{\eta^*max}$ temperature difference (°C) versus the molecular weight (g/mol) for the commercial plasticizers studied (data for phthalates from ref. 3), excluding the polymeric adipates.

helps plastisols withstand the stresses evolved caused by the gas released during the decomposition of chemical blowing agent (CBA); this leads to foams of better quality and more homogeneous bubble size distribution.

The corresponding data are shown in Table III, along with the $\eta^*$ values at the different temperatures studied. It was also observed (see the foam quality discussion section of this article) that the best quality foams were generally provided by plastisols presenting the highest $T_{ADC} - T_{\eta^*max}$ values among all of the plasticizers studied, for example, DHA (54°C), ATBC (46°C), and ASE (61°C). Considering these temperature difference values in the case of phthalates, we observed the same trend, as the best quality foams were provided by plastisols of diethyl-phthalate (DEP) and di-isobutyl-phthalate (DIBP) (with difference values of 95 and 84°C, respectively).

Figure 3 shows the $T_{ADC} - T_{\eta^*max}$ temperature difference values against the molecular weight for all 20 plasticizers studied in the previous part I of this series and in this part, except for the polymeric adipates. A linear correlation was observed between
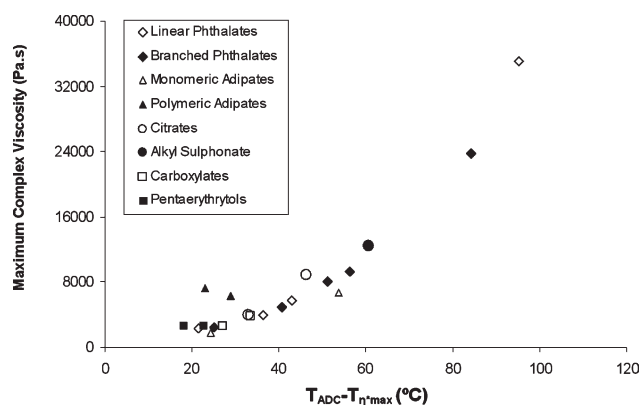
these two parameters (especially when the different plasticizer families were considered). The two polymeric adipate plasticizers departed from this trend more strongly than the two pentaerythytols esters of fatty acids.

Figure 4 shows the maximum complex viscosity ($\eta^*_{max}$) values against the $T_{ADC} - T_{\eta^*max}$ of the corresponding formulations. The trends discussed within each family could be clearly seen.

In Figure 5, the same parameter is shown, however, in this case, against the molecular weight of the plasticizer, and the polymeric adipates were also excluded for better comparison. The correlation with the difference of temperatures $T_{ADC} - T_{\eta^*max}$ seemed to be clearer than with the molecular weight, and even the polymeric adipate type plasticizers were closer to the general trend in this plot as compared with the molecular weight plot. It was apparent that the $T_{ADC} - T_{\eta^*max}$ temperature difference was a parameter more representative of the behavior of the system than the molecular weight itself because it combined two other parameters related to the degree of development of the structure of the plastisols more closely than the molecular weight did.

## Evolution of the extensional viscosity

Studying the extensional flow[29,30] of polymer melts is extremely important because of the industrial relevance in most of the polymer transformation processes[31] (e.g., blow molding,[32] fiber spinning,[33] extrusion,[34,35] injection molding,[36] foaming[7,12,37,38]). In a previous article,[3] we studied and discussed the plasticizer influence on the elongational behavior of plastisol formulations prepared with nine phthalate ester type plasticizers. It was found that plasticizers followed similar behavior with the molecular weight as described for $\eta^*$; the plastisols of higher molecular weight plasticizers developed higher extensional



**Figure 4** $\eta^*_{max}$ (Pa s) values at the $T_{ADC} - T_{\eta^*max}$ temperature difference (°C) for the 20 commercial plasticizers studied (data for phthalates from ref. 3).



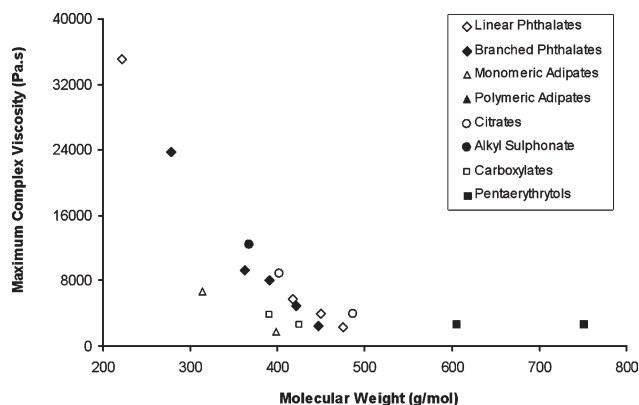**Figure 5** $\eta^*_{max}$ (Pa s) versus the molecular weight (g/mol) for the commercial plasticizers (data for phthalates from ref. 3) studied excluding the polymeric adipates.
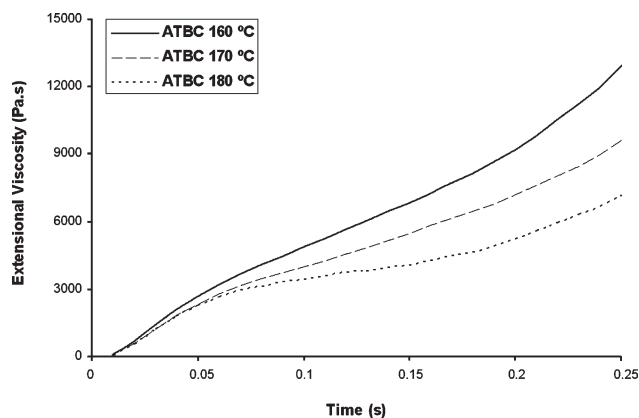
**Figure 6** Evolution of the extensional viscosity (Pa s) of the plastisol prepared with the ATBC plasticizer at 160, 170, and 180°C measuring temperatures.

viscosities. However, this relation was not as clear as in the case of $\eta^*$. Furthermore, the extensional viscosity decreased with temperature, as expected, and the shear thickening[39] seemed also to decrease with the temperature. This was in good agreement with the results reported by Sugimoto[40] in the study of the rheological properties of PVC-plasticized systems and the relation with the extensional viscosity. Figure 6 shows the extensional viscosities of the previously cured (at 180°C for 10 min) samples prepared with ATBC under the following measuring conditions: a 0.1-s$^{-1}$ prestretch, a 5-s$^{-1}$ extensional rate, and three temperatures, 160, 170, and 180°C. This is shown as an example of the trends shown by the 11 plasticizers studied. In this case, when we studied 11 different plasticizers of six chemical families, the same conclusions could be deduced, as in the case of the phthalates. Because all of the curves obtained presented similar trends, to compare and discuss the results, we decided to analyze the extensional viscosity values obtained at 0.2 s in the extensional experiment.

Table IV shows the summary of these data, and Figures 7–9 show the corresponding graphs at the three temperatures studied and for all of the plasticizers (monomeric adipates, citrates, carboxylates, pentaerythrytols, and the alkyl sulfonate) studied.

In Figures 7, 8, and 9, it can be observed that generally, the extensional viscosity decreased with the temperature. Furthermore, the extensional viscosity increased with the molecular weight of the plasticizer used. All of the plasticizers followed this trend; however, ATBC and DHA had abnormal behavior, which can clearly be seen in Figures 8 and 9. This could have been due to the high volatility of these two plasticizers, as discussed in the case of $\eta^*$. ATBC and DHA were the two plasticizers with the lowest boiling points (327 and 315°C, respectively) of the 11 studied in this work. Consequently, plasti-

cizer losses were likely to occur when we obtained the different test specimens studied, depending on the processing conditions. In the extensional viscosity measurements, the plasticizer evaporation was even more probable because the samples prepared to such measurements were precured at 180°C for 10 min in an open mold. A further reason was that these samples were measured at elevated temperatures (160, 170, and 180°C) during a longer period of time (including the preconditioning of the samples). A similar situation was observed in a previous study[3] in the determination of the extensional viscosity of plastisols prepared with DIBP and DEP, although in that case, the effect observed was even more marked than in this case. This was in good agreement with the very low boiling points of these two plasticizers (i.e., DIBP at 327°C and DEP at 299°C).

Thus, to obtain reliable results, the actual amount of plasticizer in the test specimen should be known. (This may not be an easy task because evaporation of the more volatile plasticizers may occur when the experiment is carried out.)

### Thermal behavior studied by DSC

The DSC thermograms of the studied plastisol formulations always presented two exothermic peaks, as in the previous systems studied.[3,13] The first one, at about 60–80°C, was probably due to the swelling of the resin, and the second one, at about 140–160°C, corresponded to the decomposition of the chemical blowing agent ($T_{ADC}$). In Table V, the two peak temperatures ($T_s$ and $T_{ADC}$), along with the corresponding involved heats, are presented.

**TABLE IV**
**Summary of the Results of the Extensional Viscosity**

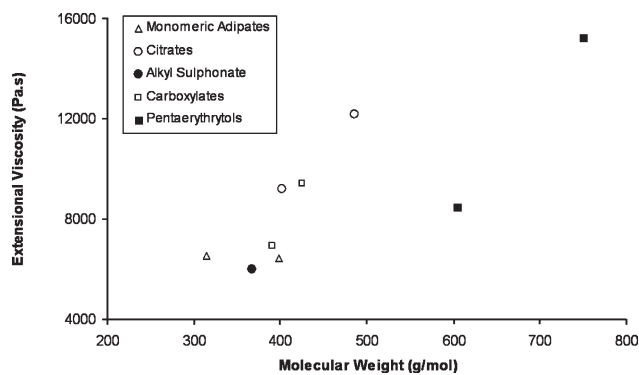| Plasticizer | Extensional viscosity (Pa s) at 160°C/0.2 s | Extensional viscosity (Pa s) at 170°C/0.2 s | Extensional viscosity (Pa s) at 180°C/0.2 s |
|---|---|---|---|
| Monomeric adipates | | | |
| DHA | 6,544 | 8,009 | 5,610 |
| DINA | 6,446 | 3,940 | 1,749 |
| Polymeric adipates | | | |
| PM 652 | 15,904 | 7,847 | 4,169 |
| PM 632 | 23,505 | 11,397 | 4,313 |
| Citrates | | | |
| ATBC | 9,189 | 7,167 | 5,188 |
| ATHC | 12,183 | 4,249 | 2,417 |
| Pentaerythrytol esters | | | |
| H 600 | 8,481 | 5,351 | 2,972 |
| H 707 | 15,240 | 8,376 | 3,355 |
| Carboxylates | | | |
| EHBDC | 6,944 | 2,685 | 1,711 |
| DINCH | 9,442 | 3,630 | 2,390 |
| ASE | | | |
| ASE | 6,021 | 3,322 | 1,401 |

**Figure 7** Extensional viscosity (Pa s) values at a 160°C measuring temperature at $0.1$-$s^{-1}$ prestretch and a $5$-$s^{-1}$ extensional rate against the molecular weight (g/mol) of the monomeric adipates, citrates, carboxylates, pentaerythrytols, and alkyl sulfonate plasticizers.

Both processes and their corresponding temperatures were strongly influenced by the type of plasticizer and its molecular weight. In the foaming process, the decomposition of the CBA had to be adequately synchronized with the viscosity evolution of the plastisol to obtain good quality foams. The temperature of the swelling of the resin increased with the molecular weight of all of the plasticizers (except for the polymeric adipates). This showed the higher compatibility of the lighter plasticizers. $T_{ADC}$ was influenced by the nature of the plasticizer and increased with the molecular weight of the plasticizer (again, except for the polymeric adipates), as we have shown in previous articles. However, samples presenting the same $T_{ADC}$ may have led to foams of very different quality. This can be explained with the different stages of the evolution of $\eta^*$ and the melt strength of the corresponding plastisol. Some plastisols at the moment of decomposition might have already developed their properties and, therefore, had the required melt strength and final structure (completely gelled) and
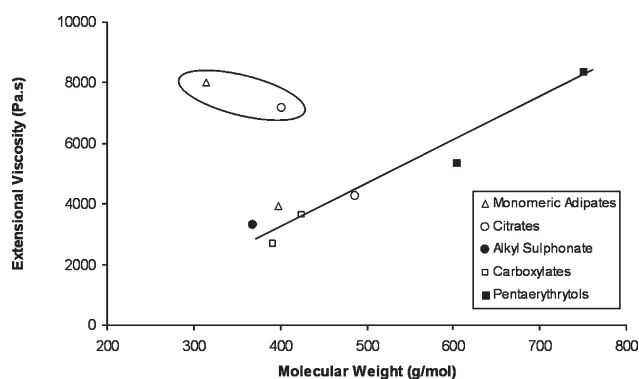
were able to provide good quality foams. Others (e.g., the plastisols of less compatible plasticizers) may not yet have finished their development, and the samples could not withstand the pressure developed by the releasing gases and, consequently, yielded poor quality foams.

### Foam characterization

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

### Resistance to penetration as studied by TMA

The resistance to penetration of the foams obtained by rotational molding was measured under the same conditions described in part I of this series.[3] As the foam production occurred in a closed mold, the foams presented similar values of the nominal density, although they differed in quality. Many of them showed very good uniformity in bubble size distribution (e.g., ASE, EHBDC, DINCH), whereas others were of poor quality and showed several types of defects (e.g., PM 632, PM 652). Uniform foams had a uniform density close to the nominal one, whereas poor foams had a nonuniform density and showed large bubbles and denser parts with larger densities than their nominal one. Large bubbles significantly affected the density of the sample. Table VI shows the density of the uniform part of the obtained foams, the measured average bubble size, and the standard deviation. These density values were used to normalize the reported TMA curves.

Figures 10 and 11 show the TMA curves of the obtained foams, normalized with the corresponding
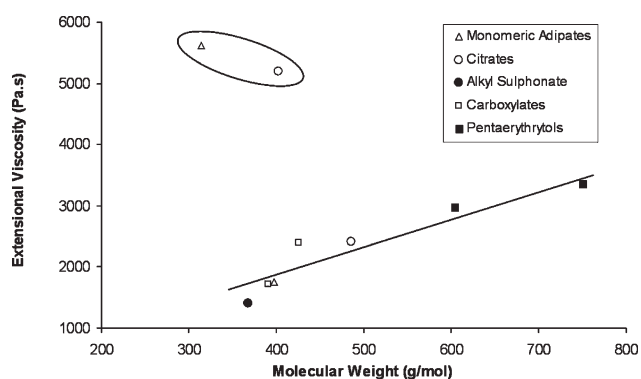


**Figure 8** Extensional viscosity (Pa s) values at a 170°C measuring temperature at $0.1$-$s^{-1}$ prestretch and a $5$-$s^{-1}$ extensional rate against the molecular weight (g/mol) of the monomeric adipates, citrates, carboxylates, pentaerythrytols, and alkyl sulfonate plasticizers.



**Figure 9** Extensional viscosity (Pa s) values at a 180°C measuring temperature at $0.1$-$s^{-1}$ prestretch and a $5$-$s^{-1}$ extensional rate against the molecular weight (g/mol) of the monomeric adipates, citrates, carboxylates, pentaerythrytols, and alkyl sulfonate plasticizers.

**TABLE V**
**Summary of the Results from DSC**

| Plasticizer | First peak temperature (°C) | First peak heat (J/g) | Second peak temperature (°C) | Second peak heat (J/g) |
|---|---|---|---|---|
| Monomeric adipates | | | | |
| DHA | 67.6 | 0.99 | 169.8 | 11.04 |
| DINA | 70.7 | 0.35 | 173.3 | 11.91 |
| Polymeric adipates | | | | |
| PM 652 | 74.0 | 0.78 | 166.8 | 8.94 |
| PM 632 | 69.2 | 0.75 | 161.3 | 8.72 |
| Citrates | | | | |
| ATBC | 66.7 | 1.03 | 167.2 | 8.91 |
| ATHC | 72.1 | 0.50 | 172.9 | 11.02 |
| Pentaerythrytol esters | | | | |
| H 600 | 72.4 | 0.52 | 170.4 | 11.94 |
| H 707 | 76.8 | 0.62 | 171.9 | 12.49 |
| Carboxylates | | | | |
| EHBDC | 72.0 | 0.18 | 175.4 | 11.49 |
| DINCH | 75.2 | 0.32 | 176.2 | 11.96 |
| ASE | | | | |
| ASE | 66.6 | 0.58 | 174.7 | 10.79 |

foam density. The softest foams (i.e., those presenting the larger dimension changes) were produced from the formulations prepared with DHA, EHBDC, and DINA. A correlation of these curves was observed with the molecular weight. Generally, the higher the molecular weight was, the higher the resistance of the sample was, as expected. However, the forthcoming foams did not follow this trend with the molecular weight, which could also be understood when we considered the fact that they had different functional groups. Nevertheless, the monomeric and polymeric adipates, as well as the carboxylates, did follow the trend within the same

family. It could also be observed that citrates presented quite similar resistance to penetration, and ASE followed the same behavior as the pentaerythrytols and had similar resistance as the citrates.

## Bubble size distribution

The bubble size distribution was obtained as described in the Experimental section. The average bubble size and the standard deviation are two parameters that are widely used to characterize the distributions and are shown in Table VI.

Figure 12 shows the average bubble size versus $T_{ADC} - T_{\eta*max}$ It could be observed that plasticizers showing higher $T_{ADC} - T_{\eta*max}$ temperature differences yielded smaller bubble sizes and more uniform foams. This could have been a consequence of the evolution of the properties of the plastisol with temperature; that is, more compatible plasticizers provided higher $T_{ADC} - T_{\eta*max}$ values; thus, they had

**TABLE VI**
**Measured Foam Density of the Final Foam, Average Bubble Size, and Standard Deviation**

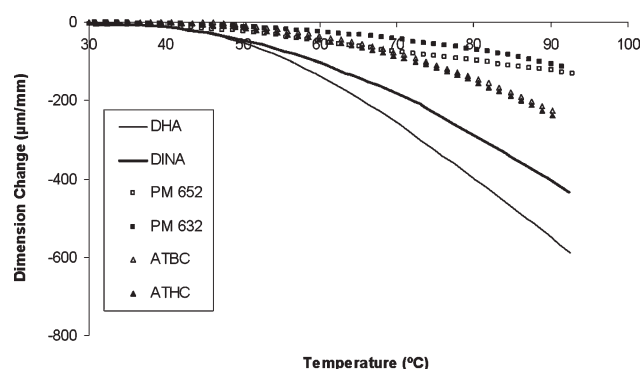| Plasticizer | Measured foam density (g/cm³) | Average bubble size (mm²) | Standard deviation (mm²) |
|---|---|---|---|
| Monomeric adipates | | | |
| DHA | 0.352 | 0.268 | 0.032 |
| DINA | 0.326 | 0.349 | 0.035 |
| Polymeric adipates | | | |
| PM 652 | 0.615 | 0.455 | 0.056 |
| PM 632 | 0.611 | 0.574 | 0.068 |
| Citrates | | | |
| ATBC | 0.325 | 0.253 | 0.027 |
| ATHC | 0.328 | 0.283 | 0.027 |
| Pentaerythrytol esters | | | |
| H600 | 0.366 | 0.321 | 0.031 |
| H707 | 0.360 | 0.376 | 0.045 |
| Carboxylates | | | |
| EHBDC | 0.247 | 0.243 | 0.022 |
| DINCH | 0.318 | 0.246 | 0.019 |
| ASE | | 0.224 | 0.020 |
| ASE | 0.350 | 0.349 | 0.035 |



**Figure 10** Resistance to penetration: adipate and citrate plasticizers.
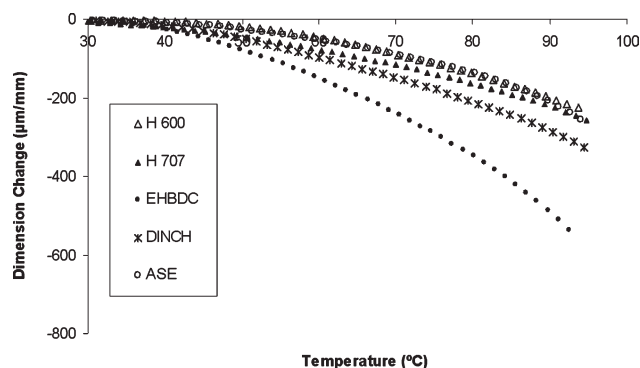
**Figure 11** Resistance to penetration: pentaerythrytol, carboxylate, and alkyl sulfonate plasticizers.



**Figure 12** Average bubble size ($mm^2$) versus $T_{ADC} - T_{\eta*max}$ (°C) in the case of all the 20 plasticizers studied.

probably already developed their final structure and properties, such as melt strength; this is important in the foaming process for the ability to withstand the pressure caused by the released gases.

### Foam morphology

In Figure 13, photographs of the foams show their morphology, the used plasticizer, the average bubble size. and the standard deviation values. As a reference, also shown is a photo of foam prepared from a widely used phthalate ester type plasticizer (DINP), which is marked with a black frame. The photographs are arranged according to the quality of the foam obtained. It could be observed that foams of the best quality (i.e., smallest average size and distribution) were those prepared with ASE, EHBDC, DINCH, DINP (from a previous work[3]), ATBC, and DHA. ASE and the two carboxylate-type plasticizers led to foams of very similar quality, and all of them provided even better foams than a widely used commercial phthalate, DINP. Thus, they can be used as plasticizer alternatives to phthalates for the process-
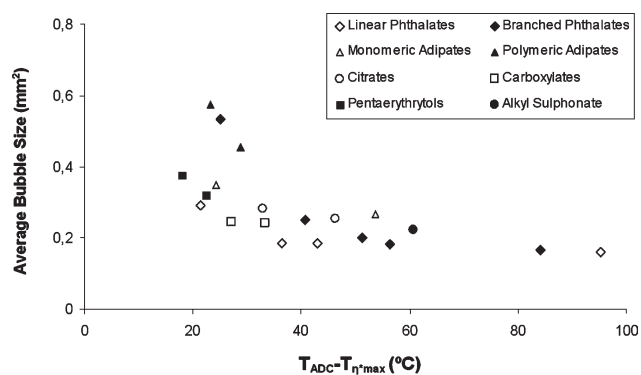
ing of good quality foams. Polymeric adipates are definitely inadequate for producing uniform foams.

### CONCLUSIONS

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

Studying the extensional viscosity of the plastisols may provide complementary information to $\eta*$ for understanding the results of the foaming process.

The temperature difference $T_{ADC} - T_{\eta*max}$ proved to be a very useful parameter for studying the foaming process because it provided a measure of the extent of evolution of the plastisol properties referred to the decomposition of the blowing agent. Plasticizers showing the largest temperature difference $T_{ADC} - T_{\eta*max}$ yielded better foams.

Characterizing the final foamed product, we concluded that the polymeric adipates were not the best option to choose for the production of uniform foams.
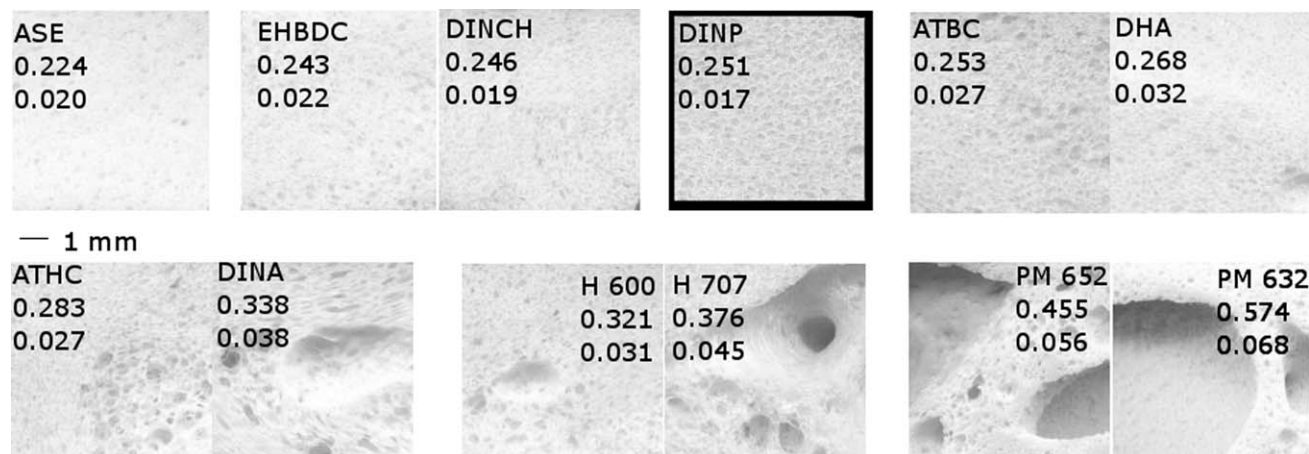


**Figure 13** Photographs of the foams obtained, presenting the plasticizer, the average cell size, and its distribution ($mm^2$), showing a reference scale of 1 mm, and a photograph of a foam prepared with the DINP commercial phthalate plasticizer.

Nevertheless, it can be emphasized that foams of very good quality were prepared with ASE, EHBDC, DINCH, ATBC, and DHA, with very similar properties to those obtained with the phthalates. Thus, according to the specific requirements for the end-use properties and depending on price and availability, these nonphthalate plasticizers can be used as valuable alternatives, especially in applications where healthy and environmentally friendly products are needed.

Consequently, as a final conclusion, we can state that knowledge of the evolution of $\eta^*$ with temperature and the blowing agent decomposition, along with the extensional viscosity, are key factors that have to be considered when one chooses a plasticizer (either phthalate or alternative) for the production of foams of required properties.

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