

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

Agnes Zoller, Antonio Marcilla

Chemical Engineering, University of Alicante, E-03080, Alicante, Spain

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ABSTRACT: The foaming of PVC (poly(vinyl chloride)) plastisols is a complex combination of simultaneous processes, involving the curing and structural changes of the plastisol, the gas generation and the foam formation. Our comprehensive study of such processes and of the influence of plasticizer on the foam quality has shown that all the processes involved have to be adequately synchronized to obtain foams of the required quality. A series of plastisols prepared by mixing a high and a low compatible phthalate ester plasticizer in several proportions (100/0, 75/25, 50/50, 25/75, 0/100 ratios) has been studied and characterized (by means of rheology, calorimetry, thermal stability, thermomechanical properties, density, and foam morphology), to study the influence of the plasticizer in such processes with changing compatibility. We found expectable rheological and calorimetric behavior regarding the plastisols without curing; however we experienced nonlinear (unexpected) behaviors in cases of foams and plastisols being cured. To confirm such behavior and our hypothesis regarding the possible plasticizer evaporation, the thermal stability of the plastisols, precured samples and foams have been studied by thermogravimetric analysis (TGA). According to our results it can be deduced that the plasticizer loss occurring in some cases during the production of the foams or the specimens being characterized, plays an important role in the foaming process and also influences the foam quality. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2691–2701, 2012

Key words: flexible PVC-VA foam; DEP-DIDP mixed phthalate plasticizers; plasticizer evaporation

INTRODUCTION

The use of foamed plastics is growing in all kinds of different applications, because they can be manufactured from many different types of polymers and their properties can be customized by adding additives^{1,2} to give specific requirements. Polymer foams are especially attractive in several areas of industry, because of their excellent properties such as light weight, low density, very good strength/weight ratio, superior insulating abilities, and energy absorption capabilities, etc. These materials are widely used in packaging, biomedicine, building, automotive, carpet underlay, textiles, furniture, or production of toys. Thus, foaming fundamentals and technology have experienced an enormous development^{3–5} in the last decades.

In our previous publications^{6–8} we provided an extensive review of the scientific literature about the production and application of polymeric foams^{5,9,10} and foaming processes.¹¹ Furthermore, we provided a better insight into the simultaneous dynamic processes occurring during foaming,^{6,8} such as gelation

and fusion¹² processes, and the swelling of the resin in the plasticizer. We studied the extensional viscosities of pastes under different processing and measurement conditions⁷ and the calorimetric behavior¹³ of plastisols which have been prepared using 20 different plasticizers. We described the correlations found between all these processes and their importance in the foaming process and foam quality.

In a similar previous publication,⁸ we studied the influence of 9 phthalate ester plasticizers towards foaming and related processes, characterized the plastisol formulations by means of rheology (complex and extensional viscosities) and differential scanning calorimetry (DSC) measurements, as well as the obtained foamed product in several aspects. As the use of the phthalate plasticizers has been questioned recently, we also carried out a similar study⁶ on plasticizers which can work as alternatives to phthalates. The melt strength^{14,15} indicates the ability of the plastisol to withstand drawing without breaking. Therefore, knowledge of its development is also crucial, because it describes how the polymer matrix withstands the stresses evolved during the gas generation and bubble growth, and stabilizes the foam structure. Thus the melt strength and extensional viscosity play a significant role in the foaming, as they are fundamental in producing low density and good cell structured

Correspondence to: A. Zoller (agnes.zoller@ua.es).

TABLE I
Properties and Suppliers of the Plasticizers Studied

Plasticizer	Abbreviation	Commercial name	Density (g/cm ³)	Boiling point atm. (°C)	Molecular weight (g/mol)	Supplier
Diethyl Phthalate	DEP	Palatinol A	1.118	298	222	BASF
Diisododecyl Phthalate	DIDP	Palatinol DIDP	0.966	420	447	BASF

foamed plastics. Obviously, these parameters are influenced by the plasticizer type, structure, molecular weight (i.e., the compatibility with the resin), so a proper selection of the adequate plasticizer for the plastisol formulations is essential to obtain the required balance of properties in the final product.

During previous research, we found very interesting results from which it can be deduced that some very compatible (i.e., those of low molecular weight within the phthalate family) plasticizers can undergo evaporation during the processing. This can be seen mainly in the extensional viscosity measurements, since the samples used were previously cured and we have proved the fact of the plasticizer evaporation by studying the thermostability of the samples. These samples have already lost a certain amount of plasticizer during the previous curing process. Consequently, in the ARES measurements they provided extremely high and unexpected extensional viscosities. We have found no reference to such possible differences between the nominal plasticizer concentration (i.e., the concentration of plasticizer used for the preparation of the plastisol) and that actually remaining plasticizer concentration in the foamed sample or cured plastisol.

Therefore, the main objective of the present publication is to focus on illustrating the dynamic complex process of foaming of reactive systems such as PVC plastisols. Moreover, to confirm the effect of the plasticizer evaporation during the curing and foaming of the plastisols occurring in open mold; to provide a feasible interpretation of the results obtained. To do so, we have selected five plastisols prepared with two very different compatibility and volatility phthalates and their mixtures in three intermediate proportions (i.e., 25/75, 50/50, and 75/25) to study the effect of the concentration on the properties of the plastisols and the quality of the corresponding foams obtained. The amount of plasticizer in the samples used for characterizing the polymer matrix as well as the foams obtained have been determined by thermogravimetric analysis to help in understanding the results.

EXPERIMENTAL

Materials

Resin

In preparing the plastisol formulations, ETINOX 400 PVC resin (E400—a vinyl chloride–vinyl acetate copolymer with a nominal 5% of vinyl acetate by AIS-CONDEL was used. Typical values provided by the supplier are 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.

Plasticizers

Table I shows the selected plasticizers, the abbreviation, the commercial name, the density, boiling point and molecular weight as well as the suppliers.

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 producers.

Methods

Plastisol preparation

Five PVC plastisols were prepared by mixing 100 phr (parts per hundred resin) of ETINOX 400, 100 phr of the plasticizers mixed in five proportions (100 phr DEP with 0 phr DIDP, 75 phr DEP with 25 phr DIDP, 50 phr DEP with 50 phr DIDP, 25 phr DEP with 75 phr DIDP, 100 phr DIDP with 0 phr DEP), 2 phr of Reagens CL4 commercial Ca/Zn-stearate stabilizer, 6 phr of Lankroflex 2307 epoxidized soybean oil as costabilizer, and 2 phr of zinc oxide as catalyst.⁸ After mixing, the pastes were subjected to a

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

TABLE III
Formulations

Formulation	Resin Etinox 400 (Phr)	Plasticizer I. DEP (Phr)	Plasticizer II. DIDP (Phr)	Stabilizer CL4 (Phr)	Co-stab. ESBO (Phr)	Kicker ZnO (Phr)	CBA ^a ADC (Phr)
100 DEP	100	100	0	2	6	2	2
75 DEP	100	75	25	2	6	2	2
50 DEP	100	50	50	2	6	2	2
25 DEP	100	25	75	2	6	2	2
0 DEP	100	0	100	2	6	2	2

^a chemical blowing agent (CBA) included in the formulations which to be foamed and for DSC measurements.

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.

Formulations

Table III shows the plastisol formulations, the components and the proportions.

Plastisol characterization

Evolution of the complex viscosity by 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⁻¹ 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 by an Ares (advanced rheometer expansion system). The extensional viscosity of $10 \times 18 \times 1$ mm³ samples, previously cured at 180°C during 10 min in an convection oven (open mold), was measured at 160, 170, and 180°C, at each temperature applying 0.1 s⁻¹ prestretch rate and 5 s⁻¹ extensional rate 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⁻¹ heating rate in Nitrogen atmosphere with a 20 cm³ min⁻¹ flow at 20°C.

Foam production

Open mold in convection oven. The freshly mixed and degassed plastisol formulations including the chemical

blowing agent (ADC) were poured into an open mold and placed into the convection oven for 10, 15, and 20 min at 180°C. The plastisol quantity and the foam weight were also measured to control the reproducibility and possible weight loss during the processing.

Foam characterization

Determination of the thermal stability of the foams and precured samples for ARES-EVF measurements by thermogravimetric analysis (TGA). Approximately 6 mg of the samples were subjected to TGA in a nitrogen atmosphere at heating rates of 5°C min⁻¹ from 30 to 600°C in a Mettler-Toledo TGA/SDTA851e/SF/1100 Thermobalance instrument. A high purity Nitrogen gas was fed at a constant flow rate of 100 cm³ min⁻¹ as inert purge gas, to avoid unwanted oxidation of the samples. The continuous on-line records of weight loss and temperature were obtained to plot the thermogravimetric (TGA) curve and the derivative thermogravimetric analysis (DTG) curves.

Determination of thermomechanical properties by thermomechanical analysis (TMA). Penetration resistance of the foams (samples processed for 15 min at 180°C open mold) was determined by using a Setaram 92-16.18 TMA instrument. Two cycles of heating were applied: the first heating cycle between 30 and 100°C at 5°C min⁻¹ heating rate in Nitrogen atmosphere without applying force; and the second heating cycle between 30 and 100°C at 5°C min⁻¹ heating rate in Nitrogen atmosphere with a 0.04N force applied.

Determination of the average bubble size and standard deviation. Images of the cross section of the foam (samples processed for 15 min at 180°C open mold) parts of ~ 1 cm were captured by a Jeol JSM-840 multi-purpose scanning electron microscope (SEM) with 75 times magnification and 15 kV accelerating voltage. Prior to the measurement, the samples were treated by Au for better observation.

Determination of the foam density. Densities of the foams prepared during 10, 15, and 20 min at 180°C in the convection oven were determined by using a Mettler-Toledo Density Kit for Analytical Balances

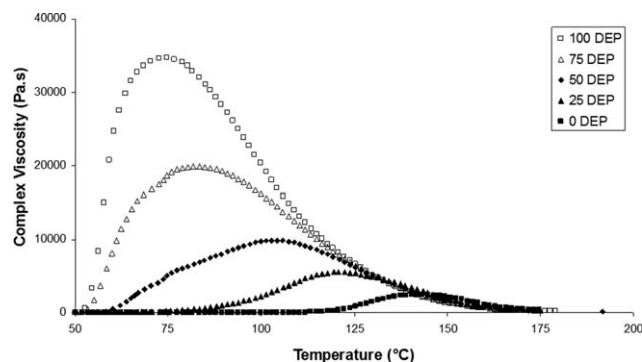


Figure 1 Evolution of the complex viscosity (Pa s^{-1}).

according to the Archimedes method. Five replicates for each sample were measured. The five stable density values were obtained in the first minute of the measurement, which led to results with a variation coefficient always lower than 1%.

RESULTS AND DISCUSSION

Plastisol characterization

Evolution of the complex viscosity

In Figure 1, a linear correlation can be observed between the more compatible plasticizer content and the gelation temperature, as well as the maximum complex viscosity. In previous publications^{8,12} we discussed the relationship between the plasticizer compatibility, molecular weight and the gelation process. We found that plastisols prepared with more compatible plasticizers have earlier gelation and develop higher complex viscosities. Furthermore, studying the complex viscosities at several temperatures between 140 and 180°C, we obtained a better understanding of the development of the final properties of each plastisols. It has been found that at a certain temperature not all the plastisols have developed their final structure and properties in the same way. Each formulation, depending on the structure and molecular weight of the plasticizer used, was found in a different stage of development of its properties and new structure. Furthermore, the developed complex viscosity becomes a linear function of the molecular weight of the plasticizer used

when the plastisol properties are fully developed. In Figure 1, it can be clearly seen that the plastisol prepared with 100 phr DEP (most compatible with PVC) reaches the highest viscosity and completes its gelation process first, while the others behave correspondingly, in good agreement with previous studies. This is a consequence of the compatibility, i.e., the more compatible plasticizers interact in a more effective way with the PVC resin.

Since one of the main objectives of the study is to analyze the plasticizer effect in the foam quality, the analysis of the complex viscosities at the decomposition temperatures of the chemical blowing agent (i.e., at the maximum decomposition rate) is very convenient to discuss the foaming processes of the pastes. The difference between the decomposition temperature of the azodicarbonamide (ADC) and the temperature of the maximum complex viscosity ($T_{\eta^*_{\max}}$) is important, since it describes the development stage of the plastisols in their viscosity, structural changes and properties during the processing. The wider this temperature range, the more developed the properties and melt strength^{14,15} of the plastisol formulations. Developed melt strength assists the plastisols in withstanding the stresses evolved by the gas generation during the foaming. The summary of the results of the complex viscosities are shown in Table IV.

Figure 2 shows the maximum complex viscosity developed and the corresponding temperature of the maximum complex viscosity against the molecular weight (i.e.: the nominal amount of DEP in the mixed plasticizer). A curved trend in both cases can be observed, especially curved at the lower molecular weights. Plastisols with lower amounts of a given plasticizer develop higher viscosities at lower temperatures than plastisols with higher plasticizer concentration. Thus, the deviation observed from the expected linear trend could be due, as we will show later, to the plasticizer evaporation, especially from those plastisols with higher DEP concentrations.

Evolution of the extensional viscosity

The knowledge of the evolution of the extensional viscosity of polymer melts is fundamental to explain

TABLE IV
Summary of the Results of the Evolution of the Complex Viscosity

Formulation	Relative molecular weight (g/mol)	Maximum complex viscosity η^*_{\max} (Pa s)	Temperature of maximum complex viscosity $T_{\eta^*_{\max}}$ (°C)
100 DEP	222	34,701	76.6
75 DEP	278	19,847	82.3
50 DEP	335	9,845	103.8
25 DEP	391	5,506	120.9
0 DEP	447	2,461	142.4

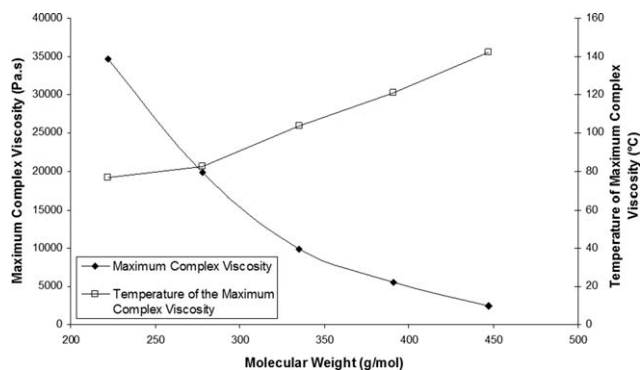


Figure 2 Maximum complex viscosity η_{\max}^* (Pa s^{-1}) and the corresponding temperature $T_{\eta_{\max}^*}$ ($^{\circ}\text{C}$) against the nominal molecular weight of the mixed plasticizer.

their foaming behavior^{15,16} and is extremely relevant in industrial processing^{17,18} especially in foaming processes.^{11,15,19,20} Numerous publications can be found dealing with the measurement of this important property and its effect in the processing. However, in the case of reactive systems such as PVC plastisols, only few references^{17,21,22} have been found. In our previous publications, we studied the effect of different plasticizers both in the shear and extensional rheology of such plastisols and found a certain correlation between the rheology and the provided foam quality of the corresponding formulations.^{6,8}

We have also found that in some cases (most volatile and most compatible plasticizers) the extensional viscosity is strikingly higher than the other cases studied. According to the literature the developed viscosity is a function of the plasticizer concentration.^{23–25} Since the preparation of the EV samples occurs in an open mold, it is very likely that the plastisol formulations depending on the plasticizer volatility may lose a certain amount of plasticizer by evaporation. Consequently, the formulations prepared with plasticizers of lower boiling points processed at 180°C oven temperature would likely contain less amount of plasticizer than the nominal one, before processing. Furthermore, samples with only DEP as the plasticizer are most probably the least plasticized ones at the moment of the experiment, thus developing the highest extensional viscosities. Furthermore, this behavior is less marked while the amount of DEP in the formulation decreases. Figure 3 shows the evolution of the extensional viscosity of the formulations measured at 160°C with 0.01 s^{-1} prestretch and 5 s^{-1} extensional rates. It can be observed that plastisols follow a general trend as the most volatile plasticizer (DEP) develops higher viscosities, while the less volatile (DIDP) reaches less extensional viscosities. A reverse trend is shown to that expected from the nominal concentration and the composition of the plasticizer used. This can be explained once again with the evaporation, as it is

possible that the plasticizer evaporation occurs even during the measurement. To confirm the plasticizer evaporation of such samples during the curing, we measured the thermal stability by thermogravimetric analyses (TGA) and in the corresponding section of the article we will report the data obtained. Hence, for the correct interpretation of the results the plasticizer evaporation has to be considered.

Thermal behavior studied by differential scanning calorimetry (DSC)

In a previous publication¹³ we have studied the influence of 20 plasticizers on the thermal transitions and related processes of the plastisols formulations. Generally, it can be observed that thermograms of the studied formulations always present two exothermic peaks^{8,13}; the first one at about $60\text{--}80^{\circ}\text{C}$ is due to the swelling of the resin, the second one at about $140\text{--}160^{\circ}\text{C}$ corresponds to the decomposition of the chemical blowing agent (T_{ADC}). These processes and their corresponding peak temperatures are strongly influenced by the type, structure and compatibility of the plasticizer. Moreover, the knowledge of the thermal behavior of these foaming systems is very important to obtain foams of required quality. In Table V the two peak temperatures (T_s and T_{ADC}) as well as the temperature difference $T_{\text{ADC}} - T_{\eta_{\max}^*}$ are presented.

In previous studies^{6,8,12,13} we have already observed that the best quality foams are generally provided by plastisols presenting the highest $T_{\text{ADC}} - T_{\eta_{\max}^*}$ values. In the present case the obtained $T_{\text{ADC}} - T_{\eta_{\max}^*}$ data are fairly linear as shown in Figure 4, in good agreement with the plastisol formulation development. However, slight deviations are once again observed for the plastisols with the higher concentrations of DEP. As Table V shows, the swelling temperature of the resin increases with the relative molecular weight. This result implies the decreasing compatibility of the plasticizer composition, when decreasing the DEP (most compatible

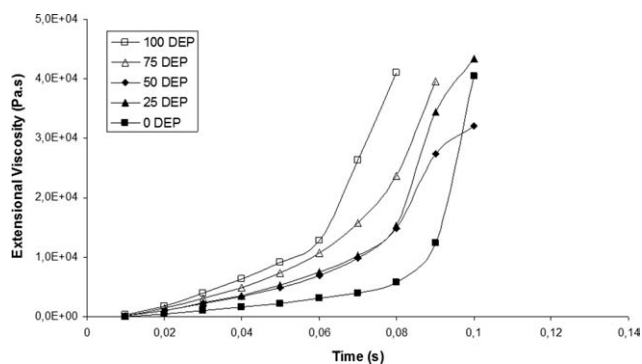


Figure 3 Evolution of the extensional viscosity (Pa s^{-1}) at 160°C .

TABLE V
Swelling Temperatures, ADC Decomposition Temperatures and Difference Between the ADC Decomposition and Maximum Complex Viscosity Temperatures of the Formulations Obtained by DSC Measurements

Formulation	Temperature of the swelling T_s ($^{\circ}\text{C}$)	ADC decomposition temperature T_{ADC} ($^{\circ}\text{C}$)	$T_{\text{ADC}} - T_{\eta^*_{\text{max}}}$ ($^{\circ}\text{C}$)
100 DEP	48.4	168.5	91.9
75 DEP	50.1	165.3	83.0
50 DEP	51.8	161.6	57.8
25 DEP	57.1	162.1	41.2
0 DEP	66.6	163.2	20.9

plasticizer) content of the formulation. This is in good agreement with earlier findings.^{8,13} The swelling temperature presents a slightly curved trend (see Fig. 4), but at such low temperatures the plasticizer evaporation is not likely to occur. Figure 5 shows the T_{ADC} versus the nominal molecular weight of the mixed plasticizer. It can also be observed that the ADC decomposition temperature values do not follow a linear trend either, as was seen in previous studies.^{8,13} In this case the evaporation of the plasticizer may also be the reason for the observed minimum, since it occurs at temperatures close to the ADC decomposition. The first process is endothermic, whereas the second is exothermic. Consequently, no linear behavior should be expected, and the presence of a minimum could be a feasible.

Thermal stability of the precured samples for ARES EVF measurements and the corresponding foams studied by thermogravimetric analysis (TGA)

To confirm the plasticizer evaporation of the samples during their processing, thermogravimetric analysis of the precured ARES samples and the obtained foamed products has been carried out. Figure 6 shows the derivative weight loss curves against the temperature in the cases of precured ARES samples. Figure 7 shows the weight loss corresponding to the last observed peak (400–500 $^{\circ}\text{C}$), i.e., that corresponding to the decomposition of the residue of the

resin.²⁶ Figure 8 shows the derivative weight loss curves against the temperature in the case of the obtained foams. Peaks below 200 $^{\circ}\text{C}$ mainly correspond to the DEP plasticizer evolution of the samples (though some DIDP evolution may also be possible at such low temperatures); furthermore some HCl or acetic acid and other resin decomposition compounds may count for part of the weight loss.^{26–29} The peaks at temperatures between 200 and 300 $^{\circ}\text{C}$ correspond to the evolution the DIDP as well as the main HCl and acetic acid evolution yielding the typical polyene residue, which decomposes at temperatures above 400 $^{\circ}\text{C}$, and is responsible for the last observed peak at about 400–500 $^{\circ}\text{C}$. In Figure 8, the DTG curve of the virgin Etinox 400 PVC-VA resin is also shown.

The effect of the presence of plasticizers and other components of the formulation (such as ZnO) on the weight loss corresponding to the first decomposition process is very remarkable. For instance, at temperatures much lower than the virgin resin alone, formulations behave showing the ZnO^{30–32} destabilizing effect.

From Figure 7, it is evident that the residue decomposed in the last step monotonically decreases with the amount of DIDP in the sample, thus proving that the corresponding sample had more plasticizer. Comparing Figures 6 and 8, it is evident that the ARES samples, also precured but not containing any CBA, loose more amount of plasticizer during the TGA measurement than the foams containing 2 phr CBA under the same measurement conditions.

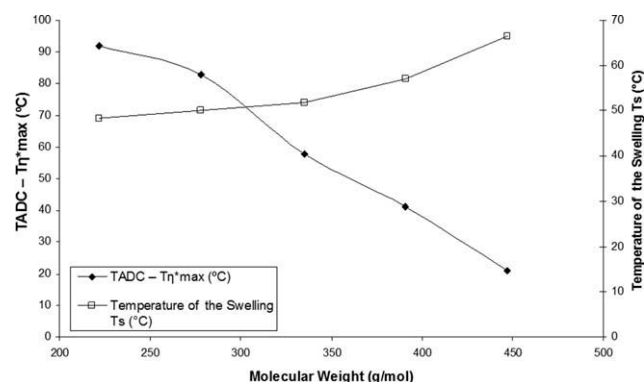


Figure 4 $T_{\text{ADC}} - T_{\eta^*_{\text{max}}}$ ($^{\circ}\text{C}$) and T_s ($^{\circ}\text{C}$) against the nominal molecular weight of the mixed plasticizer.

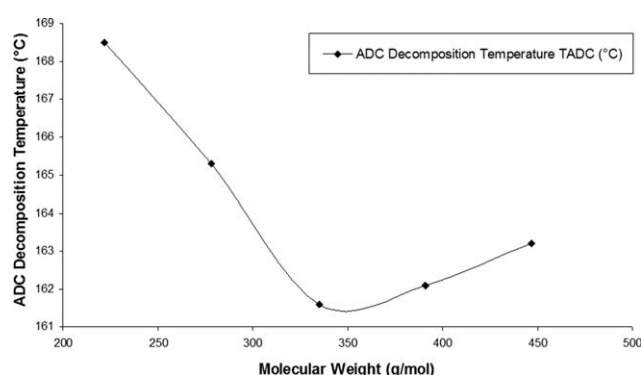


Figure 5 ADC decomposition temperature T_{ADC} ($^{\circ}\text{C}$) versus the nominal molecular weight of the mixed plasticizer.

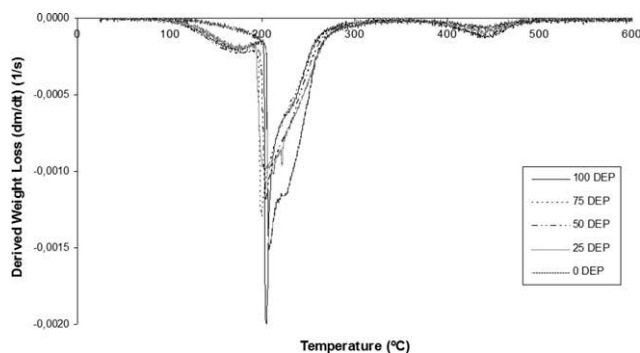


Figure 6 Derivative weight loss curves versus temperature of the ARES-EVF samples.

In the case of the foams, the first peak observed, mostly ascribable to the DEP, allows an estimation of the amount of plasticizer remaining in the foam obtained. Considering that the plasticizer with DIDP has no plasticizer loss, this estimation (i.e., subtracting to all samples at 195°C the weight loss at that temperature obtained in the sample with only DIDP), is shown in Figure 9.

To demonstrate the behavior of the formulations studied in a clearer way, the following figures present the comparison of the precured ARES samples and foams. Figures 10–12 show the derivative weight loss curves of 3 formulations: the 100 DEP, 50 DEP, and the 0 DEP (i.e., 100 DIDP). In Figure 10, it can be observed that the formulation of 100 DEP processed at 180°C for 10 min (without containing CBA) losses a large amount of the DEP plasticizer content. However, the same formulation containing CBA processed under the same conditions losses much less plasticizer. This result reveals that during the foaming process as gas generation also occurs, the released gases and the bubble formation hinder the eventual plasticizer loss. Moreover, the ADC also affects the peaks corresponding to the residue, as in all cases these peaks appear later than in the case of the formulations that do not contain ADC. These results can be observed in all the curves obtained.

Figure 11 shows the case of the formulations prepared with 50 phr DEP and 50 phr DIDP. In this case the difference is not as high as in the first case

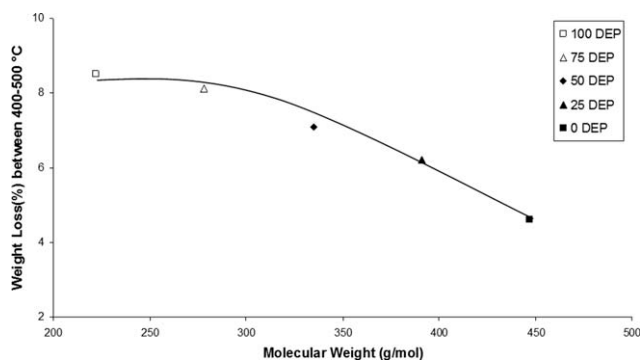


Figure 7 Weight loss values of the ARES-EVF samples between 400 and 500°C versus molecular weight.

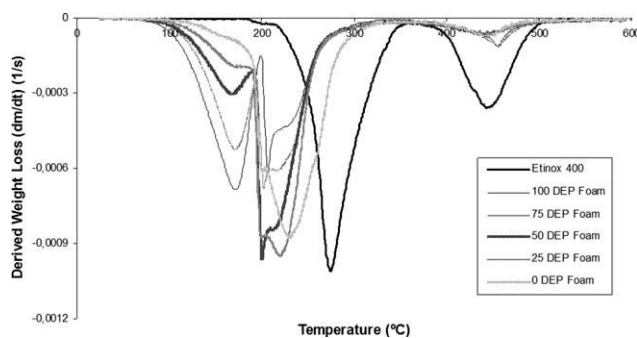


Figure 8 Derivative weight loss curves versus temperature of the obtained foams and the pure Etinox 400 PVC-VA resin.

discussed, but it can still be observed that the foam has lost less amount of plasticizer during the processing because of the foaming process.

The same tendency can be observed in Figure 12 showing the corresponding curves of the formulations prepared with 0 phr DEP (and 100 phr DIDP). Since DIDP plasticizer is the least volatile (boiling point: 420°C), this plasticizer hardly evaporates from the formulation during the processing. For this reason, in the range of 100–200°C the plasticizer loss is hardly observable. Nevertheless, a modification of the shape of the peaks is observed showing also the effect of the chemical blowing agent. Other interactions between the components of the formulations such as plasticizer/ZnO or resin/CBA may be responsible for the observed behavior.

Foam characterization

Resistance to penetration studied by thermomechanical analysis (TMA)

Resistance to penetration of the foams obtained in the convection oven in an open mold, was measured under the conditions described above and in part I⁸ and II.⁶ Figure 13 shows the curves obtained. A first insight reveals quite erratic behavior of this variable.

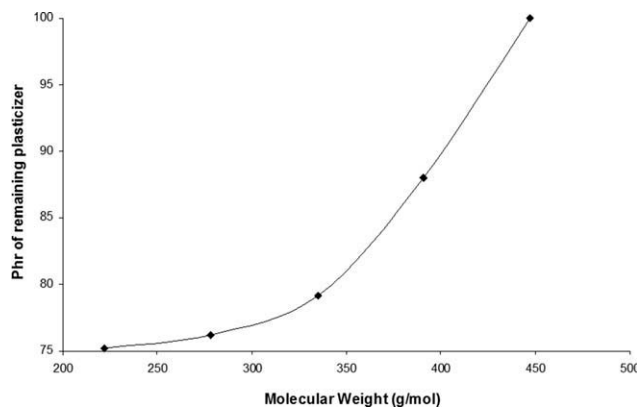


Figure 9 Phr of remaining plasticizer as a function of the nominal molecular weight of the mixed plasticizer.

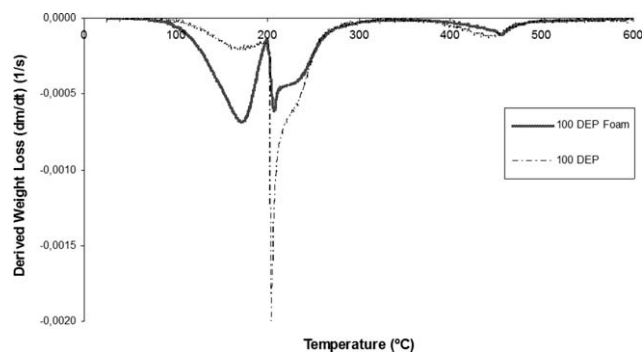


Figure 10 Comparison of the derivative weight loss curves versus temperature of the formulations prepared with 100 phr DEP.

Nevertheless, it must be considered that not all the foams have the same amount of plasticizer and also the molecular weights of the plasticizers are very different. Taking into account these observations, the results can be explained. The sample initially containing 100 phr of DEP is the one having less amount of plasticizer after processing but also the lowest molecular weight. Thus it showed low resistance at low temperatures (soft). The foam obtained of 100 phr DIDP contains the highest amount of plasticizer after processing which leads to a highly plasticized product, but this plasticizer has also the highest molecular weight. This results in soft behavior at low temperatures but with a slope decreasing at higher temperatures. Further, the initial positive values of this formulation may be due to the dilatation of the sample that remains hard enough to compensate the pressure applied by the test probe. The other formulations in between, have intermediate amounts of plasticizer and average molecular weights, thus exhibiting correspondingly intermediate behaviors.

Foam morphology by scanning electron microscopy (SEM) and determination of the bubble size distribution

The bubble size distribution has been obtained as described in the experimental section. The average

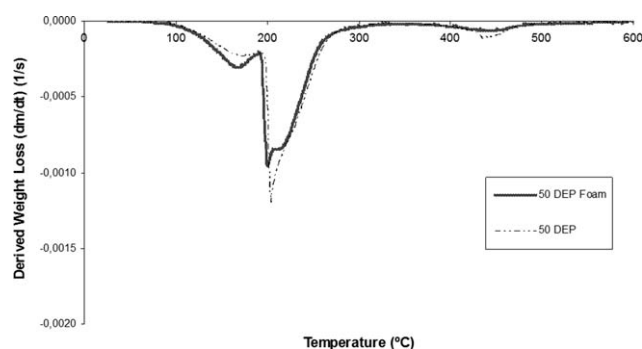


Figure 11 Comparison of the derivative weight loss curves versus temperature of the formulations prepared with 50 phr DEP and 50 phr DIDP.

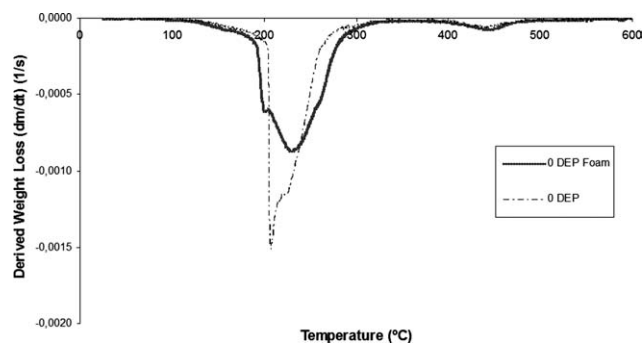


Figure 12 Comparison of the derivative weight loss curves versus temperature of the formulations prepared with 0 phr DEP (i.e., 100 phr DIDP).

bubble size and the standard deviation are two widely used parameters to characterize the distributions. The morphology of the foams can be observed in the SEM images of each foam and finally a cumulative distribution of the series is presented.

Figure 14 shows the SEM image of the foam prepared with 100 DEP. It can be observed that the bubbles are very symmetric and round which means that the plastisol withstood the pressure evolved by the released gases during the foaming and so has developed required properties at the moment of the gas generation.

Figure 15 shows the SEM picture obtained in the case of 75 DEP formulation. It can be seen that these bubbles are generally larger than in the previous case. This means that the foaming process in this case developed a little more effectively, and thus also had more bubble area and less wall area than in the other case (see data in Table VI).

Figure 16 shows the SEM picture obtained of the foam of 50 DEP formulation. It can be observed that the morphology of the corresponding foam is similar to the foam prepared with the formulation of 75 DEP; however it seems to have a bit higher standard deviation. This observation is in good

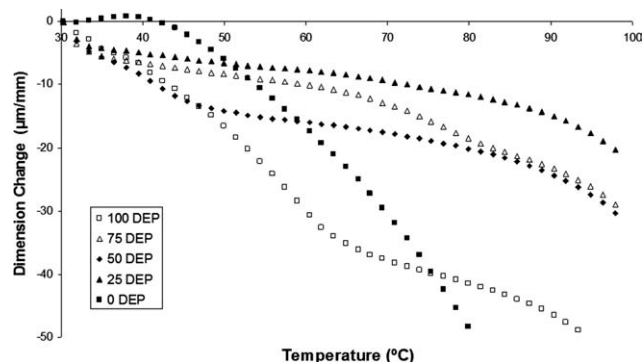


Figure 13 Resistance to penetration of the foams obtained.

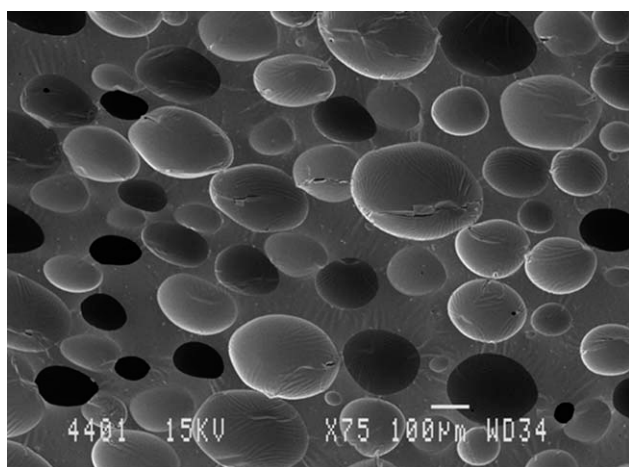


Figure 14 SEM image of the foam prepared with 100 phr DEP.

agreement with the statistics results obtained, presented below.

Figure 17 shows the SEM picture obtained of the foam of 25 DEP formulation. This foam presents a rather inhomogeneous morphology comparing it to the others obtained, as it can be clearly observed that both the cell form and size differ from the others previously mentioned. In this case the formulation only contains 25 phr of DEP which means that the nominal molecular weight of the plasticizer mixture is also higher. Observing the obtained image, we can see more large bubbles than small ones. This formation can be explained by the decreasing compatibility of the plasticizer mixture with the resin used, and thus the resin particles and the plasticizer interact in a less effective way. Therefore, the paste also develops its rheological properties in a different way, which in turn leads to a foam of distinct properties and quality.

The last SEM image (Fig. 18) shows the morphology of the foam obtained containing only DIDP plasticizer. Similarity with the 25 DEP formulation can be observed, i.e., increasing DIDP concentration in the formulation leads to foams of poorer quality, for the same reasons as in the previous case. The plasticizer compatibility and molecular weight influence the development of the plastisol, which plays a role in the foam formation during the gas generation and foaming. Pastes such as 100 DIDP (i.e., 0 DEP) undergo their structural changes in a

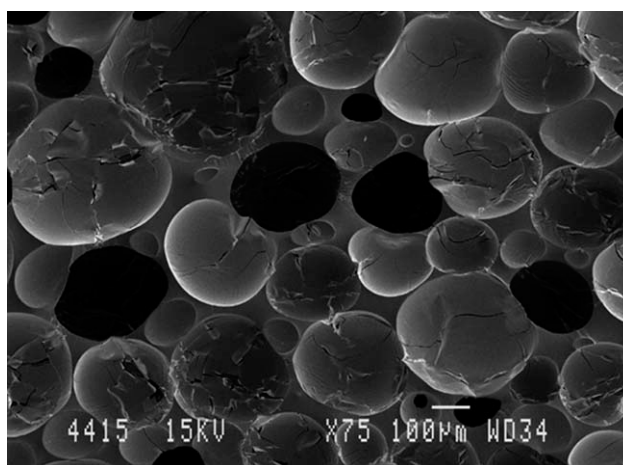


Figure 15 SEM image of the foam prepared with 75 phr DEP.

different way, and thus, even this plastisol has foamed well, their bubbles are broken which is again, related to the plastisol structural and melt property development.

In Table VI, we present the obtained data related to the foam morphology, i.e., the average bubble size and the standard deviation, the total bubble area, wall area and the bubble proportion of the studied area.

According to our results, the average bubble diameter of the foams obtained is ~ 0.2 mm, with a standard deviation of 0.1 mm. Moreover, the most foamed products are those having the highest bubble area values, i.e., the foams of mixed plasticizers including both the DEP and the DIDP, where the combination of the real amount of plasticizer present and its compatibility are likely to develop the adequate melt strength to withstand the gas generation and expansion process letting the growth of the bubbles without causing their collapse.

In Figure 19 the cumulative distribution of the foam series can be easily observed.

Foam densities obtained by Mettler-Toledo density kit for analytical balances

The densities of the foams obtained, after processing the plastisol formulations containing 2 phr ADC as CBA at 180°C processing temperature for 10, 15, and 20 min of processing time, are shown in Table VII.

TABLE VI
Summary of the Foam Properties

Formulation	Average diameter (mm)	Average bubble size (mm ²)	Standard deviation	Total bubble area (mm ²)	Wall area (mm ²)	% Bubble area
100 DEP	0.145	0.0166	0.0662	2.464	1.091	69.3
75 DEP	0.187	0.0273	0.0838	3.082	0.474	86.7
50 DEP	0.187	0.0275	0.0969	3.025	0.530	85.1
25 DEP	0.256	0.0515	0.1373	3.369	0.187	94.7
0 DEP (100 DIDP)	0.204	0.0327	0.1029	1.986	1.569	55.9

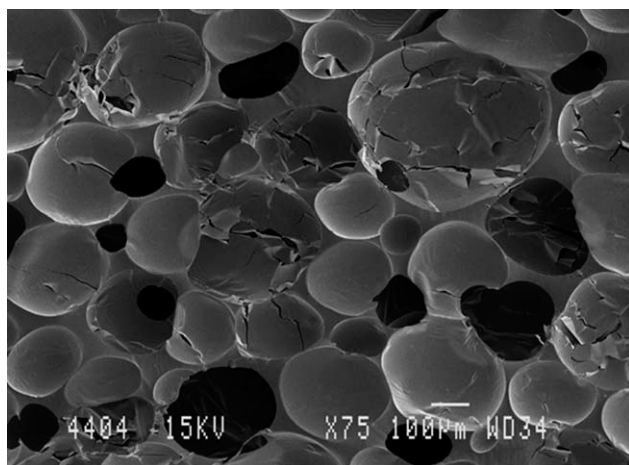


Figure 16 SEM image of the foam prepared with 50 phr DEP.

The preparation of the foams during different time intervals is very convenient to illustrate the foaming development. Figure 20 shows the densities of the foams obtained during a period of 10, 15, and 20 min. In the case of 10 min it can be deduced that this processing time is not enough for the studied formulations to be perfectly foamed, as the density values are $\sim 0.5\text{--}0.8\text{ g cm}^{-3}$.

The densities obtained during 15-min processing time reveal that the densities are significantly lower than in the previous case, as the plastisols have foamed in a more effective way. It can be observed moreover, that the tendency is not linear however this could be expected from the nominal formulations. This also confirms the plasticizer evaporation during the processing, as the 100 DEP and 0 DEP formulations provide foams of similar densities, which is a clear confirmation of the DEP loss in the formulation. This way, the 100 DEP finally contains less plasticizer than the nominal, which causes the same effect as a less compatible plasticizer without

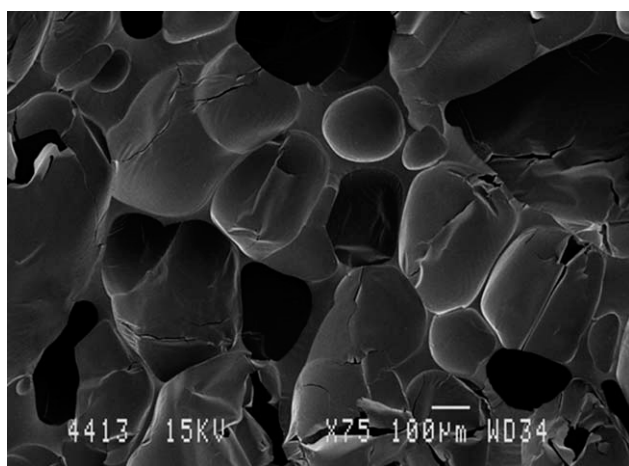


Figure 17 SEM image of the foam prepared with 25 phr DEP.

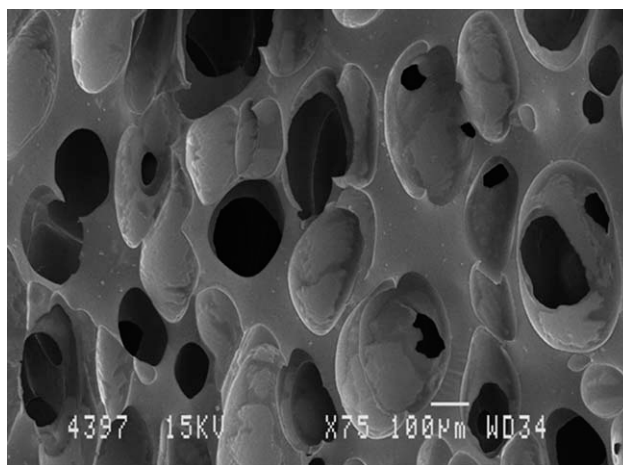


Figure 18 SEM image of the foam prepared with 0 phr DEP (100 DIDP).

evaporation. The mixed formulations provided the lighter foams, and obviously these are the foams which developed better foaming.

In the case of 20-min processing time similar density values can be observed. This result implies that all these formulations studied processed during a period of 20 min could provide similar foams. However, in some cases some slight burn and darker tone were observable on the surface of these foams, which means that some decomposition took place.

It can be deduced that the optimal processing time in the case of the studied formulation is between 15 and 20 min, as during this time intervals most plastisols can provide very low density foam. Under the conditions used, 10 min is obviously not enough for these formulations to be processed and to maximize their foaming, as the densities of the obtained foams are still too high. It can also be observed, that densities obtained for 15 and 20 min are very similar in almost all the cases, except for the 100 phr DEP formulation. The most foamed products are obtained with the 20-min processing time, however in some cases some slight burn can be observed. Thus, the recommended processing

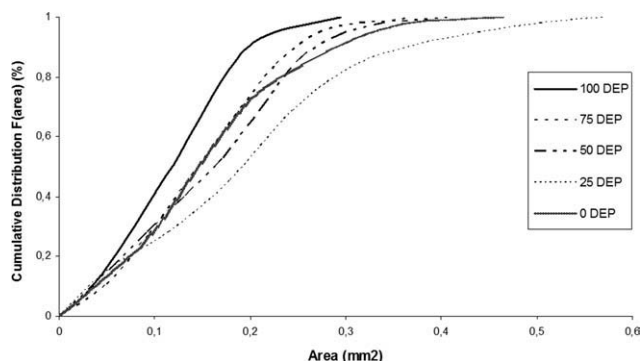


Figure 19 Cumulative distribution of the foams obtained.

TABLE VII
Summary of the Densities Measured of the Obtained Foams

DEP phr	DIDP phr	Density (10 min)	Density (15 min)	Density (20 min)
100	0	0.837	0.482	0.261
75	25	0.582	0.320	0.291
50	50	0.657	0.264	0.252
25	75	0.499	0.280	0.245
0	100	0.512	0.350	0.337

time for these formulations and process conditions at 180°C would be about 17–18 min.

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.
- Characterizing the plastisols, we observed that some formulations depending on the plasticizers used can undergo a plasticizer evaporation process which may lead to the false interpretation of the results especially of the ARES EVF measurements. This kind of plasticizer loss during the processing of the studied formulations has not been explicitly reported before; however it is strongly recommended that this fact be considered.
- Characterizing the final foamed products, it can be emphasized that foams of similar quality can be prepared by mixing two plasticizers of completely different volatility and compatibility.
- Consequently, as a final conclusion it can be stated that the consideration of the plasticizer evaporation during the processing of the formulations is of crucial importance, to interpret the

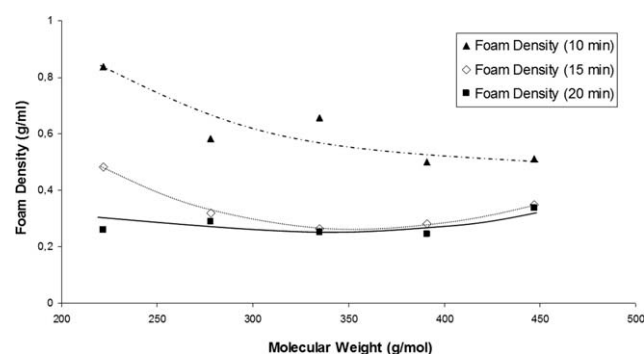


Figure 20 Densities of the foams obtained for 10, 15, and 20 min processing time against the DEP proportion of the corresponding formulation.

results and obtain a better insight of the behavior of these complex processes.

References

1. Titov, W. V. PVC Plastics; Elsevier Applied Science: New York, 1990.
2. Gächterand, R.; Müller, H. Plastics Additives Handbook: Stabilizers, Processing Aids, Plasticizers, Fillers, Reinforcements, Colorants for Thermoplastics; Carl Hanser: Munich, 1993.
3. Baldwin, D. F.; Tate, D.; Park, C. B.; Chaand, S. W.; Suh, N. P. J Jpn Soc Polym Process 1994, 6, 187.
4. Baldwin, D. F.; Tate, D.; Park, C. B.; Chaand, S. W.; Suh, N. P. J Jpn Soc Polym Process 1994, 6, 245.
5. Suh, K. W.; Park, C. P.; Maurer, M. J.; Tusim, M. H.; Genova, R. D.; Broosand, R.; Sophiaea, D. P. Adv Mater 2000, 12, 1779.
6. Zoller, A.; Marcilla, A. J Appl Polym Sci 2011. DOI: 10.1002/app.34108.
7. Zoller, A.; Marcilla, A. J Appl Polym Sci, Unpublished results.
8. Zoller, A.; Marcilla, A. J Appl Polym Sci 2011, 121, 1495.
9. Saha, M. C.; Mahfuz, H.; Chakravarty, U. K.; Uddin, M.; Kabirand, M. E.; Jeelani, S. Mater Sci Eng A 2005, 406, 328.
10. Lee, R.; Lanier, C. W.; Broemmelsiek, E. H. Production of Foamed Polymer Structures, 1989. U.S. Pat. 4804504 Available at: <http://www.freepatentsonline.com/4804504.html>.
11. Rosato, D. V.; Rosatoand, D. V.; Rosato, M. V. In Plastic Product Material and Process Selection Handbook; Elsevier: Oxford, 2004; p 333.
12. Marcilla, A.; Zoller, A. J Vinyl Additive Technol, to appear.
13. Zoller, A.; Marcilla, A. J Appl Polym Sci, to appear.
14. Ruinaard, H. J Cell Plast 2006, 42, 207.
15. Wang, J. Rheology of Foaming Polymers and Its Influence on Microcellular Processing, Doctoral Thesis, University of Toronto, Department of Mechanical and Industrial Engineering; 2009.
16. Ramesh, N. S.; Lee, S. T. J Cell Plast 2000, 36, 374.
17. Petrie, C. J. S. Extensional flows. In Rheology Series; Signer, D. D. K. D.A., Chhabra, R. P., Eds.; Elsevier: Oxford, 1999, 8, p 613.
18. Petrie, C. J. S. J Non-Newtonian Fluid Mech 2006, 137, 1.
19. Mills, N. J. In Polymer Foams Handbook; Butterworth-Heinemann: Oxford, 2007; p 39.
20. Kozłowski, M.; Szczurek, S.; Szczurek, T.; Frackowiak, S. Int J Mater Form 2008, 1, 751.
21. Everitt, S. L.; Harlen, O. G.; Wilson, H. J.; Read, D. J. J Non-Newtonian Fluid Mech 2003, 114, 83.
22. Macosko, C. W. Rheology: Principles, Measurements, and Applications; VCH: New York, 1994.
23. Garcia, J. C.; Marcilla, A. Polymer 1998, 39, 3507.
24. Marcilla, A.; Beltrán, M. Polym Degrad Stabil 1998, 60, 1.
25. Aouachria, K.; Belhaneche-Bensemra, N. Polym Degrad Stabil 2006, 91, 504.
26. Chirinos-Padrón, A. J.; von Schoettler, G. A. Polym Degrad Stabil 1991, 33, 213.
27. Marcilla, A.; Beltrán, M. Polym Degrad Stabil 1996, 53, 251.
28. Beltrán, M.; Marcilla, A. Polym Degrad Stabil 1997, 55, 73.
29. Jiménez, A.; Iannoni, A.; Torre, L.; Kenny, J. J Therm Anal Calorimetry 2000, 61, 483.
30. Ahmad, Z.; Manzoor, W. J Therm Anal Calorimetry 1992, 38, 2349.
31. Rodolfo, A.; Innocentini Mei, L. H. J Appl Polym Sci 2010, 118, 2613.
32. Manzoor, W.; Yousaf, S. M.; Ahmad, Z. Polym Degrad Stabil 1996, 51, 295.