

DSC Study of Foamable Poly (vinyl chloride-co-vinyl acetate) Plastisols of Different Commercial Plasticizers

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ABSTRACT: In this article the characterization of the thermal behavior of foamable PVC (Poly (vinyl chloride)) plastisols from 20 different plasticizers has been studied by differential scanning calorimetry (DSC). The interactions between the resin and the plasticizer as well as the decomposition of the azodicarbonamide (ADC)—the chemical blowing agent (CBA) used—have been analyzed. The latter process is of crucial importance for the knowledge of plasticized PVC flexible foam formation. Clear effects of the

chemical nature of the plasticizers and their molecular weight (M_w) have been observed, both in the interactions (swelling and early stages of gelation) between the resin and the plasticizer, as well as in the temperature of the ADC decomposition and the shape of the DSC peak. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3314–3321, 2011

Key words: DSC; PVC; chemical blowing agent; decomposition; characterization

INTRODUCTION

The plasticized PVC is one of the most useful polymeric materials at industrial scale, because of its processability, wide range of obtainable properties and low cost. In 2001, the world consumption of PVC was around 25 million t, second in ranking only after low density polyethylene. In China, PVC consumption in 2001 was 4 kg per capita, in 2006 8 kg per capita and it is expected to rise to 11 kg per capita in 2011. Based on European and US figures, PVC consumption seems to be continually increasing.¹

PVC is a widely used material in different applications such as packaging, toys, building, biomedicine, automotive, and in various other fields. There are also several types of applications such as flexible PVC foams, because of their light weight, excellent strength/weight ratio, superior insulating abilities and energy absorbing performance. Mechanical properties of foamed polymers change with different additives.² Foams can be flexible or rigid,³ due to their glass transition temperature (T_g), which in turn depends upon chemical composition, the degree of crystallinity and the degree of crosslinking. According to their cell geometry,⁴ foams can be opened or closed cell. The opened cell foams are generally flexible while the closed cell ones are generally rigid.^{5–7}

A further parameter is the foam density, which depends on the fillers and additives.

There are several possibilities in foam production,⁸ but in general two methods of foaming process are used.

1. Physical methods: Introduction of the gas (e.g., CO₂)⁹ or a volatile chemical compound, expands or volatilizes on processing;
2. Chemical methods: based on the formation of gas during foaming¹⁰ by decomposition of a chemical blowing agent (CBA) such as azodicarbonamide (ADC)—used in our case—at elevated temperature or by a chemical reaction of the components.

PVC plastisols^{11,12} are suspensions consisting of particles of a PVC resin in a liquid continuous phase, formed mainly by a plasticizer and a stabilizer. By heating at about 180–200°C, the plastisol mixture undergoes two transformation processes called gelation and fusion.^{13,14} The PVC particles and plasticizer fuse together and form a homogeneous material. These widely described processes can be monitored by a various techniques,^{15–17} but mainly by determining rheological properties^{18–24} such as the evolution of the complex viscosity of the pastes with temperature by a dynamic Bohlin rheometer.^{13,14,25–29}

To produce foams, ADC² is generally added to the plastisol formulation, which decomposes by heating.³⁰ This complicates the understanding of the foam formation processes, since these

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transformations cause the variation of all the plastisol formulation properties and structure over time. These processes can be followed and described by differential scanning calorimetry (DSC),^{31–33} which is a powerful widely used technique to study the different phase transitions, such as melting, glass transitions, or exothermic decompositions undergone by polymers. These transitions involve energy or heat capacity changes that can be detected by DSC with great sensitivity.

Since PVC undergoes dehydrochlorination³⁴ by heating, heat stabilizers such as Ca/Zn stearates^{35–38} or organotin³⁹ compounds should be added. Stabilizers also affect the rate of decomposition of the chemical blowing agents.

Previous works studied the DSC behavior of different PVC pastes as well as the kinetics of the transitions involved in the thermal treatments of polymers,⁴⁰ binary mixtures of polyethylene (PE) and (ethyl vinyl acetate) EVA copolymer⁴¹ and ternary mixtures of EVA, PE, and ADC.^{42,43} Other DSC studies of PE and EVA⁴⁴ and foamable mixtures⁴⁵ were also carried out. Important effects and interactions between the different components of the formulations were observed including also the crosslinking process.^{45,46}

The interactions between the plasticizer and the resin during the curing process⁴⁷ are very well known and the modification of the T_g of the resin as a consequence of the presence of the plasticizer⁴⁸ and the thermal effects during the swelling⁴⁹ and curing^{50,51} of the resin have been described in the literature.^{52,53} Nevertheless we have found no paper dealing with the heat effects involved in the swelling of the resin by different plasticizers and the effect of the nature of the plasticizer.

Thus, the objective of this work is to study the thermal transitions during the processing of foamable plasticized PVC-VA plastisols, including the thermal effects involved in the swelling of the resin and in the ADC decomposition, considering the effect of the chemical nature and molecular weight (M_w) of the plasticizer.

EXPERIMENTAL

Materials

Plasticizers

In a previous study a series of 20 commercial plasticizers from various chemical families was selected to study the influence of the plasticizer on the rheology.⁵⁴ In this article we have used the same 20 plasticizers to study the thermal transitions, including the decomposition of the ADC, of the corresponding PVC (with 5% vinyl acetate) pastes. Table I shows the plasticizers selected, the type or chemical family,

the abbreviation used, the commercial name, the density and the molecular weight (M_w) as well as the manufacturer.

As the main object of the study was the production of very soft foams for toy applications, a plasticizer concentration of 100 phr (per hundred resin) was consequently selected.

Resin

The PVC resin ETINOX 400 (E400, which is a vinyl chloride-vinyl acetate copolymer with a nominal 5% of vinyl acetate, typical values provided by the supplier are 4.8% of comonomer and a K value of 70) by AISCONDEL was used to prepare these plastisol formulations.

This resin was chosen to study the effect of the type of plasticizer, since a previous series of experiments revealed that plastisol formulations prepared with the E400 resulted in the best flexible foams, with an appropriate appearance and bubble size distribution.

Chemical Blowing Agent and Stabilizers

In these plastisol formulations we used: azodicarbonyl amide (ADC) D 200 A (by UNICELL) as the chemical blowing agent; CL4 Commercial Ca/Zn stearate (by REAGENS) and Lankroflex 2307 epoxidized soybean oil (by AKCROS CHEMICALS) as stabilizers, and zinc oxide (by PANKREAC) as the kicker.

METHODS

Twenty PVC plastisols were prepared by mixing the E400 resin with the blowing agent (2 phr), the kicker (2 phr), the stabilizer (2 phr), the costabilizer (6 phr) and each one of the 20 different plasticizers selected (100 phr). After mixing, the pastes were subjected to a degassing process for 15 min with a maximum vacuum of 1 mbar for air removal. Thermal transitions of the paste, 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.

RESULTS AND DISCUSSION

Figure 1 shows the DSC corresponding to the resin Etinox 400 (E400) from 50 to 100°C. The T_g (determined, according to Berhstein⁵⁵ as the midpoint of the inflection observed in the corresponding DSC trace) of the resin can be observed at temperatures around 81.4°C (in good agreement with other authors⁵⁶ who obtained a T_g of 81.7°C when studying the blends of this resin with EVA).

TABLE I
Properties and Producers of the Plasticizers Used

Plasticizer	Abbreviation	Commercial name	Density (g/mL)	Molecular weight (g/mol)	Producers
Linear Phthalates					
Diethyl Phthalate	DEP	Palatinol A	1.118	222	BASF
Heptyl nonyl undecyl phthalate	HNUP	Palatinol 711-P	0.971	418	BASF
Nonylundecyl Phthalate	NUP	Palatinol 911-P	0.958	450	BASF
Diundecyl Phthalate	DUP	Palatinol 11	0.953	475	BASF
Branched Phthalates					
Diisobutyl Phthalate	DIBP	Palatinol IC	1.039	278	BASF
Diisooheptyl Phthalate	DIHP	Jayflex 77	0.991	362	Exxon
Diethylhexyl Phthalate	DOP	Palatinol DOP	0.983	391	BASF
Diisononyl Phthalate	DINP	Palatinol N	0.973	421	BASF
Diisodecyl Phthalate	DIDP	Palatinol DIDP	0.966	447	BASF
Adipates					
Dihexyl Adipate	DHA	Plastomoll DHA	0.935	314	BASF
Diisonoyl Adipate	DINA	Plastomoll DNA	0.922	398	BASF
Polymeric esters of adipic acid					
Polymeric esters of adipic acid	PM 652	Palamoll 652	1.050	3300	BASF
Polymeric esters of adipic acid	PM 632	Palamoll 632	1.145	7000	BASF
Citrates					
Acetyl tributyl citrate	ATBC	Citroflex A4	1.050	402	Morflex
Acetyl trihexyl citrate	ATHC	Citroflex A6	1.050	486	Morflex
Others					
Mixture of alkylsulfonic phenyl ester	ASE	Mesamoll ASE	1.055	368	Bayer
Bis(2-ethylhexyl)-1,4-benzenedicarboxylate	EBDC	Eastman TM 168	0.984	391	Eastman
Di(isononyl) cyclohexane-1,2-dicarboxylate	DINCH	Hexamoll DINCH	0.949	425	BASF
Pentaerythritol esters of fatty acids	H 600	Hercoflex 600	1.000	604	Hércules
Pentaerythritol esters of fatty acids	H 707	Hercoflex 707	1.000	750	Hércules

Figure 2 shows two consecutive scans from 40 to 200°C of one of the plastisols studied in the present work (i.e., that prepared with DEP). Two clear features can be observed in the first scan. The first one, occurring at temperatures around 50°C corresponds

to the interactions of the plasticizer and the resin causing an exothermic peak due to the swelling and early gelation stages of the resin.^{29,53} The second one corresponds to the ADC decomposition resulting in another exothermic peak at temperatures around

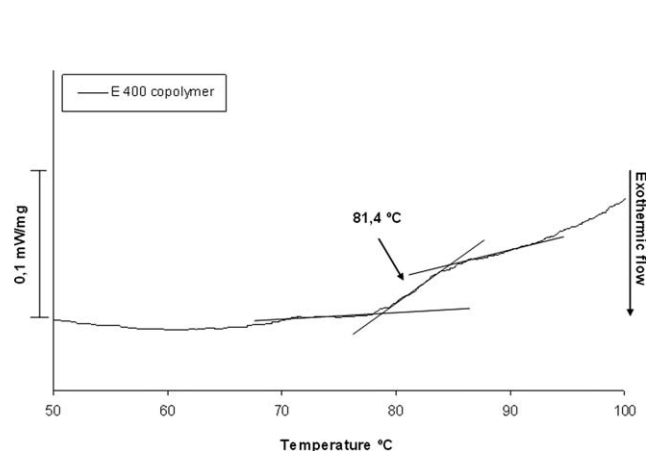


Figure 1 DSC of the Etinox 400 Poly(Vinyl Chloride-co-Vinyl Acetate) resin.

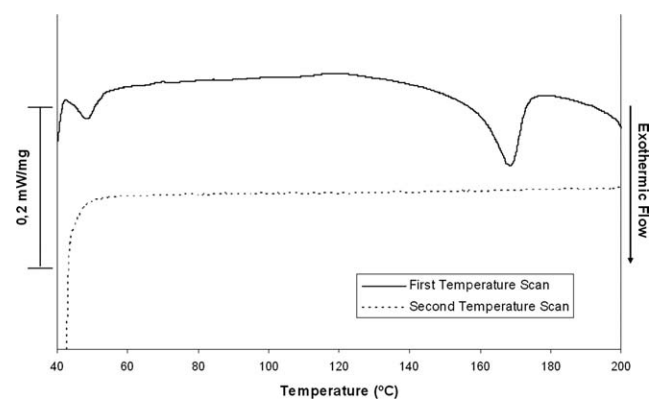


Figure 2 Two consecutive temperature scans (DSC) of the plastisol prepared with the Etinox 400 Poly(Vinyl Chloride-co-Vinyl Acetate) resin and Diethyl-phthalate (DEP) plasticizer.

TABLE II
Heat and Peak Temperatures Corresponding to the First and the Second Peaks, Temperature Where the Area Under the Second Peak is 5% of the Total Area and $\Delta T = T(2)-T(5\%)$ of all the 20 Plastisols Studied

Plasticizers	First peak temperature T(1)/(°C)	First peak heat H(1)/(J/g)	Second peak temperature T(2)/(°C)	Second peak heat H(2)/(J/g)	Temperature at 5% area of the second peak T(5%)/(°C)	$\Delta T = T(2)-T(5\%)$ $\Delta T/(^{\circ}\text{C})$
Linear Phthalates						
DEP	49,4	1,84	169,6	12,39	148,9	20,7
HNUP	70,0	0,74	175,0	10,95	157,5	17,5
NUP	73,9	0,33	178,4	10,32	163,5	14,9
DUP	74,4	0,38	175,4	12,43	157,0	18,4
Branched Phthalates						
DIBP	60,6	3,24	171,4	11,94	164,1	7,3
DIHP	67,9	0,82	175,4	11,58	164,1	11,3
DOP	69,5	0,84	176,3	11,22	152,6	23,7
DINP	71,8	0,52	174,8	10,84	159,5	15,3
DIIDP	67,3	0,50	166,0	11,88	137,3	28,7
Adipates						
DHA	67,6	0,99	169,8	11,04	156,1	13,7
DINA	70,7	0,35	173,3	11,91	156,3	17
PM 652	74,0	0,78	166,8	8,94	149,5	17,3
PM 632	69,2	0,75	161,3	8,72	143,1	18,2
Citrates						
ATBC	66,7	1,03	167,2	8,91	150,3	16,9
ATHC	72,1	0,50	172,9	11,02	156,6	16,3
Others						
ASE	66,6	0,58	174,7	10,79	160,9	13,8
EHBDC	72,0	0,18	175,4	11,49	154,7	20,7
DINCH	75,2	0,32	176,2	11,96	154,4	21,8
H 600	72,4	0,52	170,4	11,94	155,7	14,7
H 707	76,8	0,62	171,9	12,49	158,1	13,8

170°C. The second scan yields almost a plane DSC curve revealing no process at all, which indicates that the interactions observed in the first scan are irreversible.

Høvik³⁰ studied the decomposition of foaming agents in PVC plastisols, and discussed only the exothermal peak of the blowing agent decomposition that presented a maximum at around 187°C. The heat evolved in this decomposition was not reported, but could be estimated from his data (samples of around 10–15 mg, a peak area of around 20 mWK, a heating rate of 10 K/min and 2 phr of ADC in a global formulation of 169 phr), as around 1000 J/g ADC. In the DSC figure reported, an exothermal peak not discussed in the original paper can be observed, at around 70°C and heat of around 0.7 J/g of plastisol is evolved. In this work, we have measured 0.83 J/g for a similar sample using a PVC-VA copolymer but with 100 phr of plasticizer instead of the 60 phr used in Høvik's article.³⁰

DSC curves corresponding to all the 20 plasticizers studied have been obtained. Table II shows the heat evolved in each process and the temperatures corresponding to the minimum of the first and second peaks, as well as the temperature where the

area under the second peak is 5% of the total area of the peak ($T(5\%)$ along with the $\Delta T = T(2)-T(5\%)$).

Further aspects that must be emphasized are the width of the second peak, corresponding to the ADC decomposition, as well as the onset, and not only the peak temperature of this process. These three aspects are very important in the foaming process since they characterize the gas evolution process in each plastisol, which must be adequately synchronized with the viscosity evolution of the paste to obtain good quality foams. Two samples with the same peak temperature may lead to very different quality foams if, for instance, in the first the ADC decomposition starts much earlier than in the second. It may be that at low temperatures the structure and/or melt strength of the first paste is not fully developed and the sample cannot withstand the pressure developed by the evolving gases. As $T(5\%)$ and $\Delta T = T(2)-T(5\%)$ give information about the width of the corresponding peak, which is considered as an important factor when discussing the foaming behavior, these temperature values have also been included in Table II, and in the following discussion of the results.

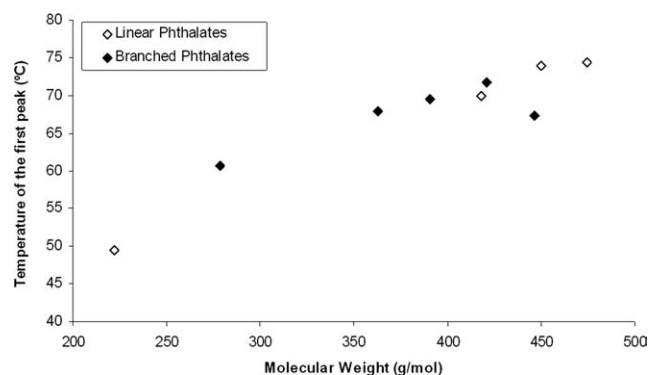


Figure 3 Temperature of the first peak versus the molecular weight of the plasticizer—linear and branched chained phthalate esters.

Figure 3 shows the temperature of the first peak versus the molecular weight of the plasticizer in the case of the phthalate ester plasticizers, both linear and branched.

All phthalate plasticizers follow an approximately linear trend; however linear chained phthalates present a somewhat lower dispersion.

Figure 4 shows the temperature of the first peak versus the molecular weight for all the plasticizers studied showing an increasing trend, except for the two polymeric plasticizers that have distinct behavior and their high molecular weight makes the interpretation of the plot difficult.

Figure 5 shows the values of the heat evolved in the first peak versus the molecular weight, excluding the two polymeric plasticizers which have values around 0.7 and 0.8 J/g of plastisol. As a general trend, it can be observed that the heat evolved decreases with the molecular weight. This trend is very clear in the case of the phthalates. The heat evolved in the case of the adipates is somewhat lower than that of the phthalates. However, phthalates present lower heat than citrates, showing a sim-

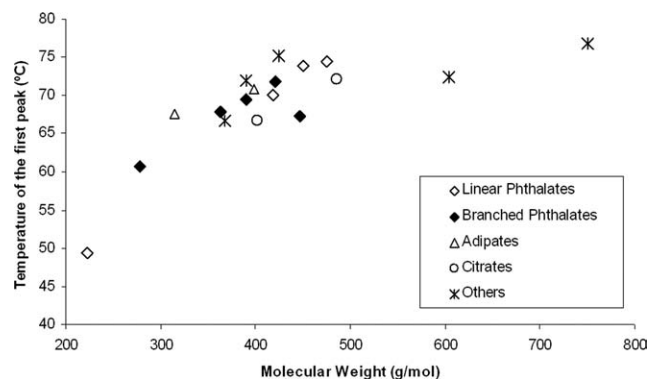


Figure 4 Temperature of the first peak versus the molecular weight for all the plasticizers used except for the polymeric adipates.

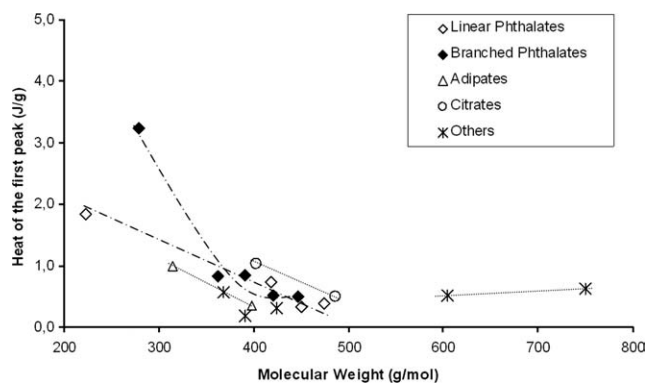


Figure 5 Heat evolved in the first peak versus the molecular weight for all the plasticizers used except for the polymeric adipates.

ilar trend to that pointed out in the case of the observed swelling temperature (see eye-guide lines on the plot). According to the literature,^{12,53,57} the molecular weight, the molecular volume, the polarity of the molecules, among other structural parameters determine the solvent power and the plasticizer compatibility with a PVC resin. Citrates have four polar groups and a tetrahedral conformation which takes up less volume and thus, these molecules result in fast incorporation into the resin. Adipates have a linear aliphatic structure and low polarity which results in a delay in the gelation process. Phthalates have an intermediate polarity due to the presence of two polar groups (thus presenting lower polarity than the citrates which have four polar groups), and their aromatic character (as compared to the aliphatic ones in the adipates).⁵⁷

The two pentaerythrytol esters (mixtures of several isomers) have the pentaerythrytol structure which has four ester groups. These groups are more separated than in the case of the citrates (five carbon atoms in the center). This, may confer more compatible behavior of such plasticizers resulting in lower temperatures and higher evolved heat, than that corresponding to the extrapolated trend observed for phthalates, adipates, and citrates.

The other two dicarboxylate type plasticizers studied (DINCH and EHBDC) have similar structures and molecular weights to the DINP. EHBDC 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, thus the corresponding evolved heat is somewhat lower. DINCH seems less compatible (from the observed swelling temperature) as a result of the lower polarity of the alicyclic structure as compared to the aromatic ring of the DINP and EHBDC. The two polymeric plasticizers are the less compatible, since they have the highest molecular weight and the lowest polarity.

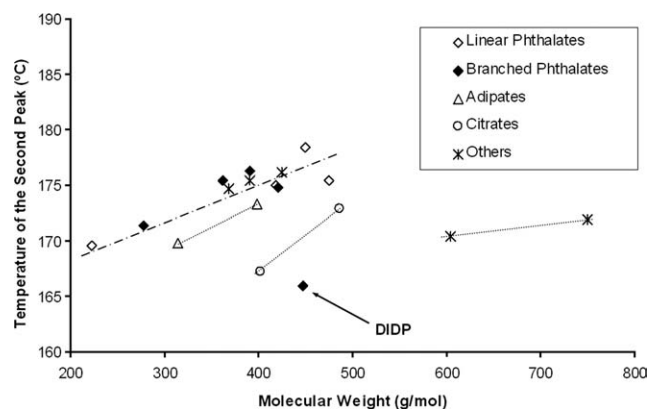


Figure 6 Temperature of the second peak (maximum decomposition rate) versus the molecular weight for all the plasticizers, except for the two polymeric adipates.

These data are in good agreement with the gelation studies carried out with these plasticizers and reported elsewhere.⁵⁴

The heat evolved in the second process corresponds to the decomposition of the azodicarbonamide. In Table II, it can be observed that most of the samples provide values around 11 J/g of plastisol. This data corresponds to around 1160 J/g of pure ADC which is consistent with the literature,⁵⁸ that reports values close to 1100 J/g for the heat of decomposition of pure ADC.

Figure 6 shows the values of the temperature of the maximum decomposition rate for all the plasticizers studied against their molecular weight, except for the two polymeric ones. It can be observed that the peak temperature increases with the molecular weight of the plasticizer. The DIDP (marked on the plot) presents abnormal behavior with respect to this trend since it provides a very low temperature of decomposition for its molecular weight. The citrates

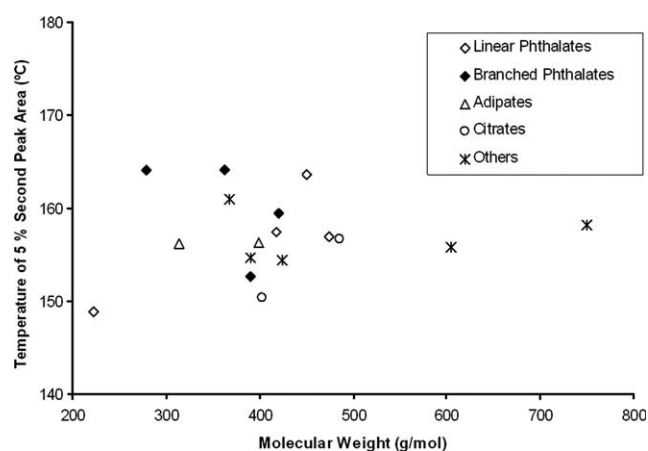


Figure 7 Temperature where the area under the second peak is 5% of the total area ($T(5\%)$) versus the molecular weight.

produce lower temperatures than the adipates and phthalates (see eye-guide lines on the plot). The rest of plasticizers produce decomposition temperatures that follow the general trend. The two pentaerythritol esters of fatty acids (M_w 604 and 750) present much lower temperatures. The two polymeric adipates follow an opposite trend to the general one, presenting decreasing temperatures with the molecular weight.

Figure 7 shows the $T(5\%)$ versus the molecular weight. In this case the correlation is not as clear as in the case of the temperature of maximum decomposition rate.

To discuss this dynamic behavior and understand the eventual foaming processes of these plastisols, it is convenient to know the evolution of the complex viscosity of the pastes during the heating process. Thus, not only the possible direct interactions of the plasticizers with the ADC, but the viscosity of the paste during the ADC decomposition should also play an important role. It must be considered that ADC is decomposing within a polymeric matrix that presents resistance to the growth of the bubbles. The melt strength may also play an important part in this process,⁵⁹ but this is out of the scope of this paper. Consequently, the higher the viscosity the higher the resistance of the matrix and the higher should be the temperature of decomposition, since the pressure inside the bubbles should grow comparatively higher.

In a previous work,⁵⁴ we studied the behavior of the complex viscosities of these pastes with temperatures under the same heating profile as in the present work. As an example, in Figure 8 we reproduce the curves obtained for the branched chained

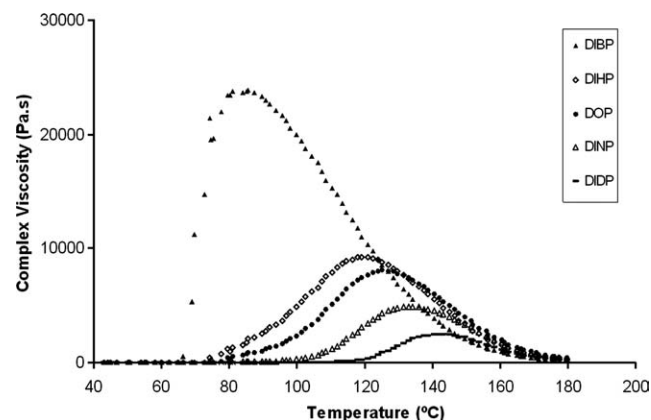


Figure 8 Evolution of the complex viscosity of the plastisols prepared with branched chained phthalate ester plasticizers. Data determined by measuring complex viscosity in dynamic oscillatory tests between 40 and 180°C at 5°C/min heating rate using 20 mm diameter parallel plates with a GAP of 0.5 mm, oscillation frequency of 1 Hz and controlled deformation of 5×10^{-3} , in a Bohlin CS 50 rheometer.

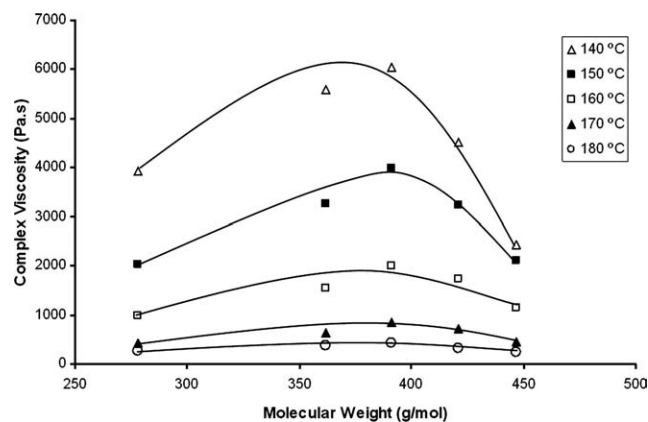


Figure 9 Complex viscosities of the plastisols prepared with branched chained phthalate ester plasticizers at 140, 150, 160, 170, and 180°C versus the molecular weight.

phthalates. Figure 9 shows the complex viscosities at 140, 150, 160, 170, and 180°C versus the molecular weight of those plasticizers. In the same previous study we concluded that the maximum of the viscosity curves was a function of the M_w of the plasticizer. Furthermore, the viscosities of the different plastisols at temperatures where they were cured (or almost developed all their properties) were also linear functions of the molecular weight of the plasticizer. Nevertheless, at lower temperatures, the less compatible plasticizers differed from this trend. This feature could be related to the fact observed in the maximum temperature of the second peak of the plastisols, that present, in general, a linear trend with their molecular weight. At this temperature, it is feasible that almost all of them have nearly completed their gelation process and have their structure and properties more developed. Thus, the viscosity of the corresponding pastes at these maximum temperatures also follows a linear trend with the molecular weight. Nevertheless, at the lower $T(5\%)$, a part of the plastisols have developed their structure, but others—the less compatible ones—are still undergoing such transformations and their strength is not yet fully developed. The high molecular weight plasticizers may have lower viscosities at the temperatures where the decomposition process of the ADC starts, and consequently may present less resistance to the decomposition process to proceed. Consequently, the $T(5\%)$ may be lower in this case than in the case of lower molecular weight plasticizers.

CONCLUSIONS

Thermal processes and behavior of PVC-VA plastisols with different commercial plasticizers including a chemical blowing agent were studied during the curing process. Two main processes have been observed, one corresponding to the interactions of

the plasticizer with the resin (swelling) and another corresponding to the decomposition of the ADC. The peak temperatures of both peaks increase with the M_w of the plasticizer.

The maximum temperature of the first peak, which corresponds to the swelling process is a nearly linear increasing function of the molecular weight, especially within each family of plasticizers. The heat evolved in the swelling process is almost a linear decreasing function of the molecular weight of the plasticizer.

The heat in the case of the adipates is slightly lower than that of the phthalates, and phthalates present lower corresponding heat than the citrates. These data are related with the compatibility of the plasticizers and agree with the literature.

The maximum temperature of the process corresponding to the ADC decomposition is an increasing function of the molecular weight of the plasticizer. The temperature corresponding to 5% of the area of the ADC decomposition peak ($T(5\%)$) is not as clearly correlated with the molecular weight of the plasticizer, showing that more complex relations must be involved at those intermediate temperatures, where the properties (i.e., the viscosity and melt strength) of the different pastes develop at different levels.

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