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Plastisol Foaming Process. Decomposition of the Foaming Agent, Polymer Behavior in the Corresponding Temperature Range and Resulting Foam Properties

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The decomposition of azodicarbonamide, used as foaming agent in PVC–plasticizer (1/1) plastisols was studied by DSC. Nineteen different plasticizers, all belonging to the ester family, two being polymeric (polyadipates), were compared. The temperature of maximum decomposition rate (in anisothermal regime at 5 K min^{−1} scanning rate), ranges between 434 and 452 K. The heat of decomposition ranges between 8.7 and 12.5 J g^{−1}. Some trends of variation of these parameters appear significant and are discussed in terms of solvent (matrix) and viscosity effects on the decomposition reactions. The shear modulus at 1 Hz frequency was determined at the temperature of maximum rate of foaming agent decomposition, and differs significantly from a sample to another. The foam density was determined at ambient temperature and the volume fraction of bubbles was used as criterion to judge the efficiency of the foaming process. The results reveal the existence of an optimal shear modulus of the order of 2 kPa that corresponds roughly to plasticizer molar masses of the order of 450 ± 50 g mol^{−1}. Heavier plasticizers, especially polymeric ones are too difficult to deform. Lighter plasticizers such as diethyl phthalate (DEP) deform too easily and presumably facilitate bubble collapse. POLYM. ENG. SCI., 53:1712–1718, 2013. © 2012 Society of Plastics Engineers

INTRODUCTION

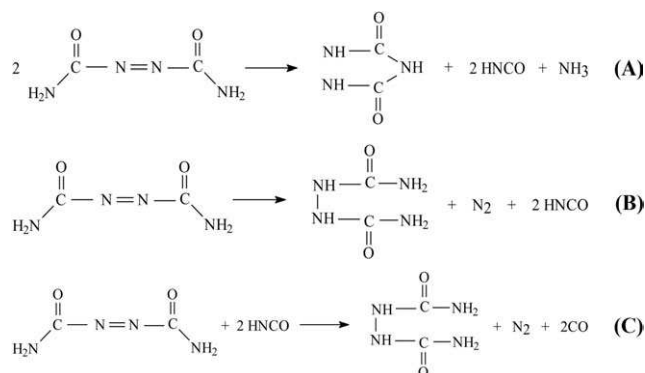
Polymer foams are products with an excellent balance of properties mainly, light weight, low density, outstanding strength/weight ratio, superior insulating abilities and energy absorbing performance. They are especially attractive in packaging, biomedicine, building, automotive, carpet underlay, textiles, furniture, shoe soles as well as the production of toys [1, 2].

The process of plastisol foaming has been widely studied [3–8] and is now relatively well understood. Foaming

can be obtained by using a chemical foaming agent [8–12] able to decompose with a high gas yield in the optimal temperature range, i.e. high enough to allow easy polymer deformation, but low enough to avoid melt fracture, bubble collapse, and other phenomena linked to low polymer elastic properties. This temperature range can be relatively sharp. In this case, the foaming agent decomposition kinetics can be critical for the process. In the present article we try to answer the following questions: To which extent does the foaming agent decomposition depend of plasticizer nature? Can we establish relationships between the plasticizer influence and its structure? Are the polymer mechanical properties at the foaming agent decomposition temperature optimal for the foaming process?

The chosen foaming agent is azodicarbonamide (ADC) which is commonly used in such applications [13]. The decomposition of ADC is exothermic, that allows using DSC for kinetic studies. Høvik [7] reported DSC heat decomposition data about ADC in PVC-DOP plastisols (60 phr against 100 here). The exotherm maximum was found at 460 K and the heat of decomposition was of the order of 1000 J g^{−1}, i.e. 116 kJ mol^{−1}.

The decomposition of the azodicarbonamide in three different reactions were first suggested by Stevens and Emblem [14] and by Lober [15] (see Fig. 1), producing a mixture of nitrogen, carbon monoxide and ammonia.



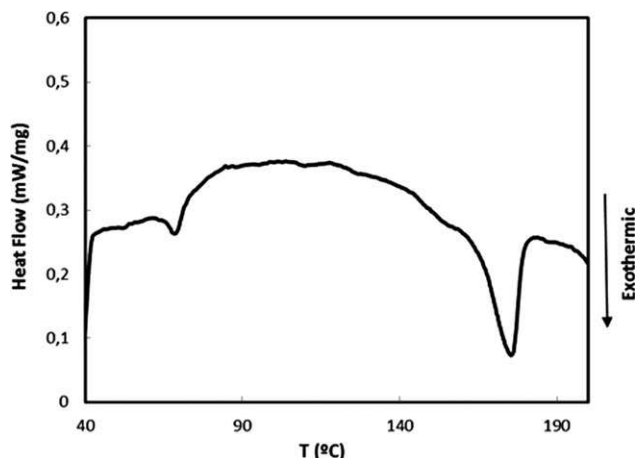


FIG. 1. Example of DSC thermogram plastisol prepared with DOP.

To our knowledge, no data are available in the literature with respect to the eventual effect of the plasticizer structure on the foaming process. This article is aimed to compare the characteristics of the ADC decomposition exotherm in 19 plastisols based on a polyvinyl chloride-poly vinyl acetate (PVC-VAC 95/5) copolymer and 19 different plasticizer of the ester family, polymer and plasticizer being in equal mass fraction in the mixture.

EXPERIMENTAL

The polymer (PVC-VAC. 95/5), its stabilizer, the foaming agent, and the plasticizers have been described elsewhere [16]. The following families of plasticizers were studied: phthalates of linear alcohols: DEP, HNP, NUP and DUP; phthalates of branched alcohols: DIBP, DIHP, DOP, and DINP; dialkyl adipates: DHA and DINA, polymeric adipates PA3 and PA7; citrates: ATBC and ATHC, pentaerythritol esters H600 and H700, and miscellaneous linear dialkyl esters/EHBDC, ASE and DINCH. Their molar mass is recalled in the tables of results. The polymer, stabilizers and blowing agents were thoroughly mixed with each plasticizer (100 phr) at room temperature in a rapid mixer at 120 min^{-1} during 5 min. Mixtures were then degassed for 15 min under vacuum (pressure $\leq 100 \text{ Pa}$).

DSC experiments were performed under nitrogen flow ($20 \text{ cm}^3 \text{ min}^{-1}$) at $5/\text{min}$ scanning rate, starting from 40°C , using a Perkin Elmer Pyris 6 apparatus.

Bulk and foam densities were measured using a Mettler-Toledo Density Kit for Analytical Balances. Appropriate sampling is crucial for determining foam densities, thus all the foam samples were cut out from the most homogeneous part of the entire foam, and replicated samples were measured.

Storage shear modulus values were determined in a Bohlin Rheometer using $a20 \text{ mm}$ diameter parallel plates with a GAP of 0.5 mm , oscillation frequency 1 Hz and controlled deformation of 5×10^{-3} , in a Bohlin CS 50 rheometer.

RESULTS

General Observations

An example of the DSC thermograms corresponding to plastisol prepared with DOP, DEP, ATBC, and DINA are shown in Fig. 1. The curves in y-axis have been arbitrarily separated to make the differences more evident. All the samples present similar behavior displaying an exotherm of which the maximum is located between 434 and 452 K , corresponding to the ADC decomposition. Additionally a minor exotherm is also evident at lower temperatures corresponding to the swelling of the resin by the plasticizer. The position and intensity of the peaks depends on the type and molecular weight of the plasticizer, as we will discuss in the present article where we focus on the ADC decomposition process. Let us recall that Høvik [7] found a value significantly higher (460 K), probably due to the different experimental conditions used (60 phr plasticizer and a temperature variation rate of 10 K min^{-1} vs. 100 phr of plasticizer and 5 K min^{-1} here). The heat of ADC decomposition was found of the order of $11 \pm 2 \text{ J g}^{-1}$, a value slightly higher than Hovik's one (9.7 J g^{-1}). Second order, although significant, variations of the exotherm characteristics can be observed from one sample to another, they will be tentatively analyzed in the following sections.

Temperature T_2 at Peak Maximum

The temperatures T_2 (Table 1) at the peak maximum vary between 434 and 451.5 K depending on plasticizer structure. T_2 was plotted against plasticizer molar mass in Fig. 2.

The points relative to polyadipates are to be considered apart. For the rest, one can distinguish four families in which T_2 increase almost linearly with M . Adipates and phthalates straight lines are almost parallel. In a first approach, it was supposed that citrates and pentaerythritol esters families are also represented by straight lines parallel to phthalate one

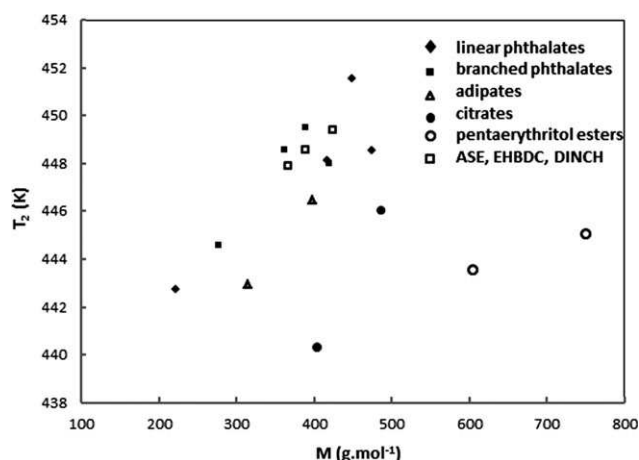


FIG. 2. Temperature at the second exotherm maximum for all the plasticizer except polyadipates vs. plasticizer molecular weight.

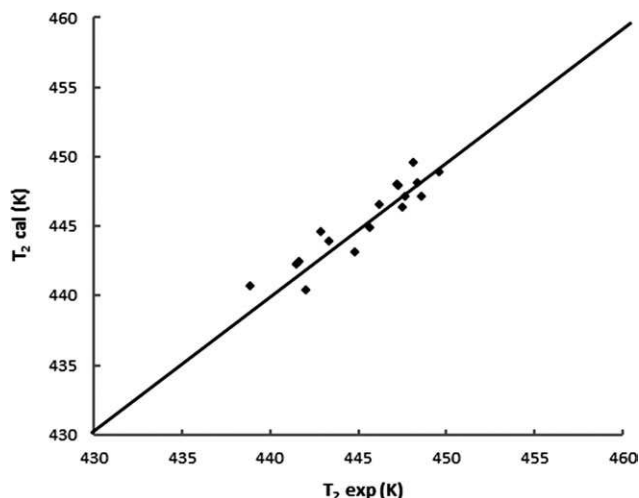


FIG. 3. Correlation between experimental and calculated values of T_2 . The straight line corresponds to equality.

and that the gap between the lines and the experimental points results only from experimental incertitude.

Then, the molar mass dependence of T_2 would be roughly represented by straight lines of equation:

$$T_2 \sim 0.0290M + T_{20} \quad (1)$$

where T_{20} values in K are 435.8 for the phthalates and ASE, EHBDC and DINCH, 433.3 for adipates, 429.0 for citrates and 422.8 for Pentaerythritol esters.

The agreement between experimental and calculated values of T_2 can be seen in Fig. 3. The adjustment of T_{20} values is, no doubt perfectible, but the chosen relationship and the corresponding parameter values are just aimed to indicate the trends of variation of T_2 . These results call for the following comments:

Although small, the variations of T_2 seem to be significant, since they allow to distinguish the plasticizer families, and to display a quasi linear dependence with molar mass in a given family.

Heat of Decomposition

H_2 (Table 1) has been plotted against T_2 in Fig. 4. H_2 appears independent of T_2 .

All the values range in the (10.3–12.5) J g^{-1} enthalpy range, except ATBC which displays a significantly lower H_2 value (8.91 J g^{-1}). It is noteworthy that ATBC displays also the lowest T_2 value.

In a given family, it is possible to distinguish a small influence of molar mass, as evidenced for the phthalates family (Fig. 5).

The point representative of DUP, visibly aberrant, has been suppressed. The dependence has been fitted by a straight-line although a small negative curvature can be distinguished (see below).

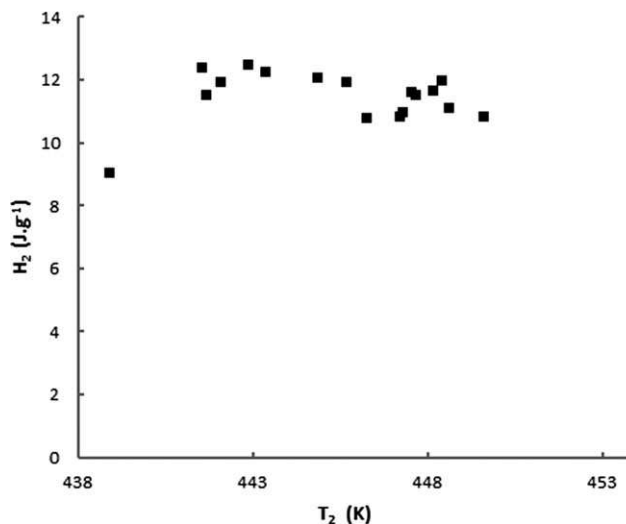


FIG. 4. Enthalpy of ADC decomposition (absolute value) against temperature for the foaming agent decomposition peak exotherm.

The number of points for each family (only 2) and the data scatter do not allow appreciating the molar mass dependence in adipates, citrates or pentaerythritols ester families.

Temperature T_5 at 5% Conversion

It has been tempted to study the difference between T_2 , corresponding to the maximum decomposition rate and T_5 corresponding to 5% conversion (Table 1). All the differences are in the 14–24 K range. The values seem to be close for certain families e.g., polyadipates (17.5 and 18.5 K), citrates (16 and 17 K), pentaerythritol esters (14 and 14.5 K). Unfortunately, in the most populated family (phthalates), the scatter doesn't allow to appreciate any eventual trend.

It has been tried to estimate the activation energy of the ADC decomposition as follows.

It is assumed to be a true first order unimolecular process of rate constant k , preexponential factor k_0 and

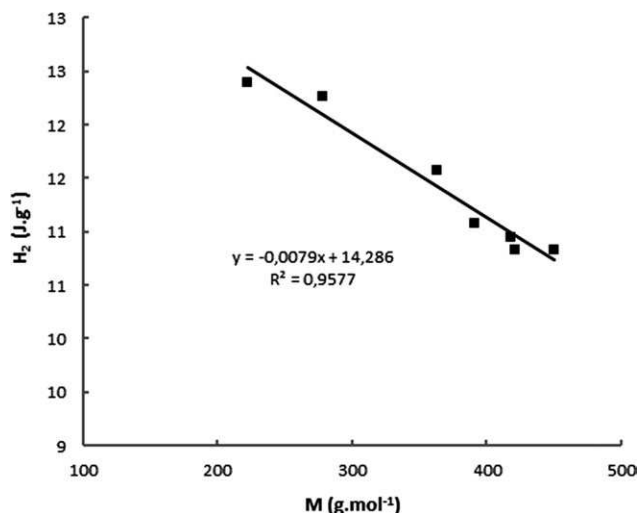


FIG. 5. Enthalpy of ADC decomposition (absolute value) against molecular weight of phthalates except DUP.

TABLE 1. Molar mass, experimental T_2 value, heat of decomposition and temperature at the onset of decomposition T_5 (K).

Name (chemical family)	Code	M (g mol ⁻¹)	T_2 (K)	H_2 (J g ⁻¹)	T_5 (K)
Diethyl phthalate	DEP	222	442.8	12.39	422
Heptyl undecyl phthalate	HUP	418	448.2	10.95	430.5
Nonylundecyl phthalate	NUP	450	451.6	10.32	436.5
Diundecyl phthalate	DUP	475	448.6	12.43	430
Diisobutyl phthalate	DIBP	278	444.6	11.94	437
Diisoheptyl phthalate	DIHP	362	448.6	11.58	437
Diethylhexyl phthalate	DOP	391	449.5	11.22	426
Diisononyl phthalate	DINP	421	448.0	10.84	432.5
Dihexyl adipate	DHA	314	443.0	11.04	429
Diisononyl adipate	DINA	398	446.5	11.91	429.5
Polyadipate	PA3	3300	440.4	8.94	422.5
Polyadipate	PA7	7000	434.5	8.72	416.1
Acetyl tributyl citrate	ATBC	402	440.4	8.91	423.5
Acetyl trihexyl citrate	ATHC	486	446.1	11.02	430
Alkyl sulfonic esters	ASE	368	447.9	10.79	434
Benzene dicarboxylate ¹	EBDC	391	448.6	11.49	428
Cyclohexane diester ¹	DINCH	425	449.4	11.96	427.5
Pentaerythritol ester	H600	604	443.6	11.94	429
Pentaerythritol ester	H707	750	445.1	12.49	431

activation energy E . C_0 and C are the concentrations at times $t = 0$ and t . The conversion ratio x is defined by:

$$x = (C_0 - C)/C_0 \quad (2)$$

$$\frac{dC}{dt} = -kC \quad \text{thus} \quad \frac{dx}{1-x} = -kdt \quad (3)$$

$$k = k_0 \exp\left(-\frac{E}{RT}\right) = k_0 \exp\left(-\frac{E}{R(T_0 + bt)}\right) = k_0 \cdot \exp\left(-\frac{E}{RT_0(1 + \frac{bt}{T_0})}\right) \quad (4)$$

T_0 is arbitrarily taken at 400 K where the conversion is negligible in the conditions under study.

The DSC scanning rate is $b = 5 \text{ K min}^{-1} = 0.0833 \text{ K s}^{-1}$

When the reaction reaches 5% conversion, $t < 8 \text{ min} = 480 \text{ s}$.

Then,

$$\frac{bt}{T_0} \leq 0.1$$

It is then licit to use the classical approximation:

$$k = k_0 \cdot \exp\left[-\frac{E}{RT_0}\left(1 - \frac{bt}{T_0}\right)\right] = k_0 \cdot \exp\left(-\frac{E}{RT_0}\right) \exp\left(\frac{Ebt}{RT_0^2}\right) \quad (5)$$

The integration of Eq. 3 leads to:

$$\ln(1-x) = \frac{k_0 RT_0^2}{Eb} \exp\left(-\frac{E}{RT_0}\right) \left(1 - \exp\left(\frac{Ebt}{RT_0^2}\right)\right) \quad (6)$$

For a true first order process, k_0 is of the order of the frequency of a molecular vibration. Let us assume that $k_0 \sim 10^{13} \text{ s}^{-1}$.

At 5% conversion, $\ln(1-x) \sim -0.05$ and the time to reach this conversion varies between 192 s (PA7) and 444 s (DIBP or DIHP). We have calculated the values of the activation energy for both extreme cases using Eq. 6. One obtains:

For PA7: $E = 130 \text{ kJ mol}^{-1}$.

For DIBP: $E = 138 \text{ kJ mol}^{-1}$.

Indeed, all the other values are in the (130–138) kJ mol^{-1} interval. It is interesting to note that this activation energy value is equal to the heat of decomposition.

Foam Density Against Shear Modulus at T_2

The foam ρ and bulk polymer ρ_p density values have been determined. From these values we have calculated the polymer volume fraction in the foam: $v = \rho/\rho_p$. All these values are listed in Table 2 with storage shear modulus at T_2 and the logarithmic derivative g' of the $G' = f(T)$ curve at T_2 .

A noticeable scatter is observed. It is presumably due to various factors such as the modulus sensitivity to temperature variations (an error of 1 K on temperature induces an error of about 10% on modulus) the possible plasticizer loss by evaporation, especially on plasticizers of low molar mass and, indeed, the incertitude on modulus measurements. Despite this scatter, one can distinguish a clear trend of v to increase with G'_{T_2} for plasticizers of high molar mass e.g. esters of pentaerythritol and polyadipates. The situation is less clear for low molar mass plasticizers but the curve seems to display a minimum around $\ln G'_{T_2} \sim 7.6$, as shown by the parabolic fit in Fig. 6.

DISCUSSION

About the Effect of Plasticizer on Decomposition of Foaming Agent

As mentioned above, there are relatively small but significant effects of plasticizer nature on ADC decomposition

TABLE 2. Code, molecular weight (g mol⁻¹), foam density ρ (g L⁻¹), polymer bulk density ρ_p (g L⁻¹), polymer volume fraction in the foam at T_2 (v^*), storage shear modulus (G' Pa) at T_2 , $g' = (1/G')(\Delta G'/\Delta T)$ at T_2 .

Code	M	ρ (g L ⁻¹)	ρ_p (g L ⁻¹)	v^*	T_2 (K)	$G'(T_2)$ (Pa)	g' (K ⁻¹)
DEP	222	343	1118	307	443	908	101
HNUP	418	278	971	286	448	2000	149
NUP	450	328	958	342	451.5	1750	-
DUP	475	342	953	359	448.5	2490	138
DIBP	278	311	1039	299	444.5	1290	108
DOP	391	333	983	339	449.5	2000	370
DINP	421	318	973	327	448	2040	116
DHA	314	352	935	376	443	812	135
DINA	398	326	922	354	446.5	1590	70
PA3	3300	615	1145	537	440	11,600	83
PA7	7000	611	1050	582	434.5	19,000	104
ATBC	402	325	1050	310	440.5	4150	337
ATHC	486	328	1050	312	446	2730	128
ASE	368	350	1055	332	448	1700	88
EBDC	391	247	984	251	448.5	2000	118
H600	604	366	1000	366	443.5	4500	114
H750	750	360	1055	341	445	6650	88

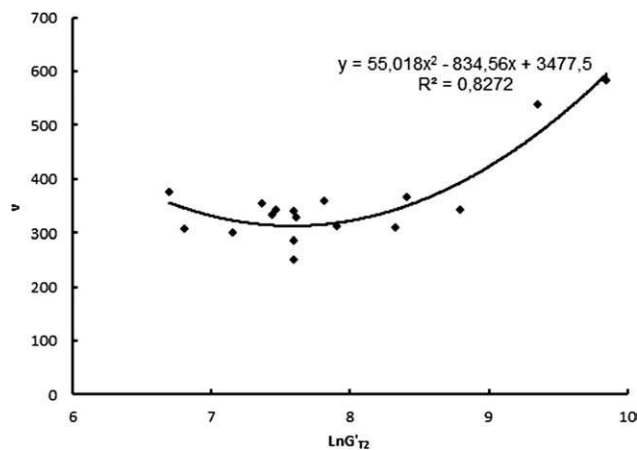


FIG. 6. Polymer volume fraction in the foam against neperian logarithm of shear modulus at T_2 .

kinetics in the plastisol matrix. A priori two kinds of effects can be expected: solvent effect and viscosity effect.

Solvent effect is mainly linked to secondary bonding between the matrix and ADC molecule. Such effects are for instance well known in the case of hydroperoxide decomposition where hydrogen bonding between the OH group and the substrate are known to accelerate the decomposition [16]. Incidentally one can remark that for hydroperoxides, as for ADC, the activation energy of their decomposition is almost equal to the dissociation energy of the oxygen–oxygen bond. In ADC, there are two NH_2 groups able to establish hydrogen bonds which, no doubt, can influence the decomposition kinetics. With plasticizers, if such interactions exist, they must involve the carbonyl ester group. The most active plasticizers from this point of view must be those having the most polar and most accessible groups, in the highest concentration. They are expected to lower the activation energy and the temperature of the exotherm onset (T_5). DEP characteristics illustrate these trends. Considerations of solvent effect could explain the difference observed between the distinct families: adipates would differ from phthalates for reasons of polarity. Citrates and pentaerythritol esters would differ from adipates for reasons of steric hindrance: certain ester groups would be partially shielded and could not be involved in interactions with ADC.

The effect of molar mass in a given family can be explained by the fact that the matrix viscosity is an increasing function of plasticizer molar mass. An increase of the medium viscosity can favor cage recombination of primary radicals and then modifies the reaction yield that could eventually explain the decrease of enthalpy with molar mass in the phthalate family.

The especially low values of H_2 of polymeric adipates PA3 and PA7 confirms the trend observed in (Fig. 5) for the phthalate family. Indeed, the viscosity of these systems is considerably higher than for all the others, cage recombinations are therefore especially favored. Do the

macromolecular plasticizers obey the same molar mass dependence as molecular ones? It seemed to us interesting to plot H_2 against $\text{Ln}M$ in Fig. 7. This figure could be interpreted as follows: the curve displays two plateaux separated by a sharp transition zone. The high exothermicity plateau, located at $H_{20} \sim 12.5 \text{ J g}^{-1}$ would correspond to low viscosity media, where no cage reactions occur. The low exothermicity plateau located at $H_{2\infty} \sim 8.5 \text{ J g}^{-1}$ would correspond to the reactions independent of cage effects. The molar mass dependence of H_2 could be tentatively represented by the following function:

$$H_2 = H_{2\infty} + \frac{H_{20} - H_{2\infty}}{1 + a\left(\frac{M}{M_0}\right)^n} \quad (7)$$

With: $H_{2\infty} = 8.5 \text{ J g}^{-1}$ and $H_{20} = 12.5 \text{ J g}^{-1}$, $a = 0.5$, $M_0 = 400 \text{ g mol}^{-1}$, $n = 4$.

The corresponding points have been plotted in Fig. 7.

M_0 would be the transition molar mass value such as for $M < M_0$ there is no cage effect, while for $M > M_0$, cage effects are fully efficient. The exponent n expresses the sharpness of the transition. These coefficient values are, indeed, only valid for the rate of temperature increase under study (5 K min^{-1}).

The low values of T_2 and T_5 are probably rather linked to a solvent effect owing the especially high concentration of unshielded esters in these polymers.

About the Relationship Between Foam Density and Polymer Modulus

As revealed by Fig. 6, there is an optimal modulus value of the order of 2 kPa, at the temperature of maximum rate of foaming agent decomposition. The curve is relatively flat in the region of this optimum showing that a relatively wide range of plasticizer molar masses, typically between 400 and 500 g mol^{-1} can display good

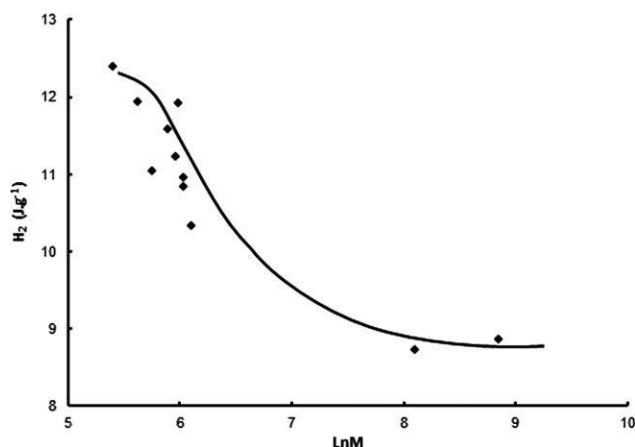


FIG. 7. Experimental and calculated (solid line, according to Eq. 7) H_2 vs. $\text{Ln}M$.

foaming performance. Indeed, the storage shear modulus can be considered only as a partial indication because high strain visco-plastic properties are presumably also involved in the foaming process, but in practice, G' can work as a suitable criterion, at least in a first approach.

The existence of this optimum can be understood as follows: for heavier plasticizers, especially polyadipates, the melt is not deformable enough at the decomposition temperature of the foaming agent. Bubbles nucleate and grow difficultly. For lighter plasticizers, for instance DHA, the melt is highly deformable, bubbles nucleate and grow easily, but they collapse not less easily, leading thus to densities higher than optimal ones.

It can be recalled that the above results are specific of the temperature ramp of 5 K min^{-1} . An increase of this rate would presumably shift the decomposition exotherm toward high temperatures, that would shift the minimum of the curve density = $f(\ln G')$ toward higher modulus values, i.e.; toward higher plasticizer molar masses.

The results are also presumably specific of the polymer molar mass. An increase of polymer molar mass would shift the curve $G' = f(T)$ toward higher temperatures, which means that melt modulus values at the foaming agent decomposition temperature would be higher, that would favor low molar mass plasticizer i.e., shift the minimum of the curve of Fig. 6 toward low modulus values.

CONCLUSIONS

This work was focused on the decomposition of azodicarbonamide in plastisol matrix, and its effects on foaming. DSC was used to determine the characteristics of the ADC decomposition exotherm. This latter begins in the vicinity of $430 \pm 10 \text{ K}$ and the heat evolved is of the order of $11 \pm 2 \text{ J g}^{-1}$, which corresponds to about 130 kJ mol^{-1} . Second order but significant variations were observed from one plasticizer to another. For a given molar mass, the maximum temperature T_2 is in the order: phthalates > adipates > citrates > pentaerythritol esters. These differences are discussed in terms of solvent and cage effects. In the phthalate family, the heat of decomposition H_2 appears as a decreasing effect of molar mass e.g.; presumably of viscosity. This trend seems to be confirmed by the especially low H_2 values observed in polymeric adipates. The shape of variation of H_2 with plasticizer molar mass suggests the existence of two asymptotic regimes: separated by a relatively sharp transition. These regimes differ by the existence (at high melt viscosities) or not (at low viscosities) of cage recombination of radicals.

Although relatively small, these differences can be critical for the process which needs a coincidence between the temperature interval of gas release and a certain range of elastic properties, in a region where they can vary rapidly with temperature.

It was found that, in the conditions under study, the efficiency of the foaming process is maximum when the storage shear modulus of the melt is of the order of 2 kPa

that corresponds to plasticizer molar mass of the order of $450 \pm 50 \text{ g mol}^{-1}$.

NOMENCLATURE

a, n	constants in Eq. 4
ADC	AzoDiCarbonamide
ASE	mixture of alkylsulfonic phenyl esters
ATBC	acetyl tributyl citrate
ATHC	acetyl trihexyl citrate
b	DSC scanning rate is (K min^{-1})
C_0 , C	concentration (mol L^{-1})
DEP	diethyl phthalate
DHA	dihexyl adipate
DIBP	diisobutyl phthalate
DIHP	diisooheptyl phthalate
DINA	diisononyl adipate
DINCH	D-isononyl cyclohexane-1,2-dicarboxylate
DINP	diisononyl phthalate
DOP	diisooctyl phthalate (diethylhexyl phthalate)
DSC	differential scanning calorimetry
DUP	diundecyl phthalate
E.	activation energy (kJ mol^{-1})
EHBD	bis(2-ethylhexyl)-1,4-benzenedicarboxylate
G'	storage shear modulus (Pa)
H_2 , H_{20} , $H_{2\infty}$	Heat of decomposition (J g^{-1})
H600	pentaerythritol esters of fatty acids
H707	pentaerythritol esters of fatty acids
HNUP	heptyl nonyl undecyl phthalate
HNUP	heptyl nonyl undecyl phthalate
k_0	preexponential factor (s^{-1})
M	molar mass (g mol^{-1})
NUP	nonyl undecyl phthalate
PA3	polyester of aliphatic dicarboxylic acids
PA7	polyester of aliphatic dicarboxylic acids
PVC	poly-vinyl chloride
t	time (s)
T	temperature (K)
T_2	temperature at peak maximum (K)
T	temperature at 5% conversion (K)
v	polymer volume fraction in the foam
VAC	vinyl acetate
x	conversion ratio (%)
ρ , ρ_p	foam and bulk polymer density (g L^{-1})

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