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Rotational Moulding of PVC Plastisol

Modelling of Initial Stages of Gelation

The viscosity during the earlier stages of the gelation process of plastisols formulated with 15 different commercial plasticizers has been obtained. Plastisols prepared were rotomoulded and mouldings obtained were characterized according to their wall thickness distribution. This parameter strongly depends on the minimum viscosity and on the rate of viscosity change during gelation (slope of the curves during the viscosity increase), and also on the temperature where no more flow of the plastisol is observed (gelation temperature). These variables are conditioned by the characteristics of the plasticizer and PVC employed, among other variables.

The effect of plate and arm velocity and rotation rate on the wall thickness distribution was also studied.

A simple model has been proposed to correlate the initial stage of the gelation of PVC plastisols formulated with the phthalate plasticizers. The suggested model assumes that the plastisol is a suspension constituted by a continuous phase (initially pure plasticizer) and a discontinuous phase constituted by PVC particles. It has been considered that the viscosity of the plastisol is influenced by the average mass molecular weight of the continuous phase and the temperature. The quantity of PVC dissolved in the continuous phase has been calculated by using a generic n -order kinetic equation for PVC dissolution rate. Additionally, a swelling process of the PVC particle by the plasticizer has also been considered and its effect on the viscosity of the suspension has also been accounted for. The model proposed provides a very good fitting of the sharp viscosity increase observed and is useful to predict the evolution of the viscosity of the parts in a rotomoulding process.

1 Introduction

In spite of PVC plastisols being the earliest liquid polymer systems to be rotomoulded and that these materials are still extensively used, the behaviour of plastisols in the mould during rotational moulding has received little attention. Powdered materials such as polyethylene are more commonly used, and consequently these systems have been largely studied.

Although some powder and liquid polymers are processed by rotational moulding, their distribution in the mould is differ-

ent. When a solid polymer is used its particles have to reach a certain temperature so that they start to attach to the mould while it is rotating. When particles become stickier, they suffer a sintering process and they join each other; by the effect of heating, air bubbles entrapped during sintering are dissolved in the molten polymer (densification process). Thus, mechanical properties of mouldings are markedly influenced by the sintering and densification steps, which actually determine the wall thickness distribution and final bubble content. Variables influencing sintering and densification have been largely studied [1 to 4].

In rotational moulding of liquid systems, as PVC plastisols, sintering and densification does not take place and the effect of oven temperature and rotation rate are different as compared to solid systems.

The changes in rheological properties of PVC plastisols as a consequence of heating have been described by Nakajima [5 to 7] and Marcilla [8 to 10]. At the beginning of the heating, the plastisol viscosity decreases, as does the plasticizer viscosity (Fig. 1). If heating progresses, a temperature is reached where the polymer starts to be swollen and dissolved by the plasticizer, causing a sharp increase in viscosity which makes it stop flowing (gelation process). Above this point, the gelation process continues causing a further increase in viscosity until a temperature where this process concludes, and the effect of temperature and fusion of the microcrystalline zones of PVC takes place, causing a drop in the plastisol viscosity. Fig. 1 shows the evolution of the complex viscosity for a plastisol of a composition typical in soft toys, as those studied in the present work.

Obviously, the distribution of plastisols in the mould is completed in the first stages of the gelation process, when the plas-

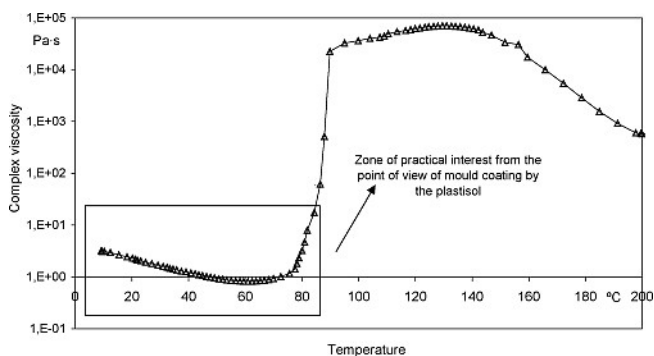


Fig. 1. Complete evolution of the complex viscosity for a conventional plastisol

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plastisol is able to flow by the effect of the low shear stress produced by the mould rotation. Under the combined effect of gravity and the draw of the mould surface, the mould surface starts to be covered by the plastisol, while some plastisol is re-pooled at the bottom of the mould. By the effect of the temperature, the plastisol at the mould surface, the plastisol at the “pool” or the plastisol flowing towards the “pool” can reach the gelation temperature and stop flowing maintaining its last position occupied when gelation occurred. Thus, under certain conditions uneven plastisol distribution in the mould, entrapped air bubbles or hydrocysts (droplets or flowing fronts of the plastisol “frozen” while flowing), can be common problems found in PVC plastisol rotomoulding [11]. The magnitude of these phenomena is dependent on processing conditions and the evolution of viscosity with temperature. The shape of this evolution, depends on the formulation used, where the type of resin and the type of plasticizer are the most significant factors to bear in mind. Although plasticizers of the phthalate type, as di(2-ethylhexyl) phthalate (DOP or DEHP) or diisononyl phthalate (DINP), have been used for decades in PVC formulations destined for the rotational moulding of toys, from the late 90’s, their utilization in PVC items susceptible to be sucked or chewed by children has been seriously questioned, mainly due to their potential carcinogenic effect. Although reports issued by NTP/NCI (National Toxicology Program, U.S.A.) [15], and the IARC (International Agency for Research on Cancer) [16] concerning the likely influence of phthalate plasticizers on humans, have not demonstrated that they are a serious risk to human health, their utilization for such purposes was banned in the European Union as a preventive measure. This measure, has therefore affected a relevant sector of the rotomoulded plastisols industry which has been forced to consider other alternatives to substitute DEHP.

In the present work the evolution of the viscosity with the temperature for plastisols formulated with 15 different plasticizers and the wall thickness distribution of rotomoulded pieces, using the same formulations have been compared. The effect of arm and plate velocity and rotation rate as well as the evolution of viscosity during the first stages of gelation on wall thickness distribution have also been studied. A simple model has been proposed to correlate the initial stages of the gelation process for the PVC plastisols of the phthalate family.

2 Experimental

All plastisols were prepared using the emulsion PVC resin Etinnox 450 from Aiscondel (E450). The average molecular weight of the PVC resin determined by Gel Permeation Chromatography in THF was 101.600.

Different plasticizers from the families of phthalates, adipates, citrates and esters were employed, which are listed in Table 1. A commercial Ca–Zn thermal stabilizer was used (Asua 656T2). The plastisols were prepared by mixing the PVC resin, 59.9 % mass fraction (65 phr, parts per hundred of resin) of plasticizer and 1.2 % (2 phr) of thermal stabilizer in a low speed mixer for 20 minutes. After preparation, the plastisols were degasified by applying vacuum for 10 min. All plastisols were stored for 7 days at room temperature before tested.

Type	Abbreviations	Supplier
Dimethyl phthalate	DMP	BASF
Dibutyl phthalate	DBP	BASF
Diisooctyl phthalate	DOP	BASF
Diisononyl phthalate	DINP	ESSO
Diheptylundecyl phthalate	PT711	BASF
Dinonylundecyl phthalate	PT911	BASF
Diundecyl phthalate	PT11	BASF
Dihexyl adipate	DHA	BASF
Diisooctyl adipate	DOA	BASF
Diisononyl adipate	DNA	BASF
Pentaerythritol ester	HER600	Hercules
Pentaerythritol ester	HER707	Hercules
Acetyltributyl citrate	ATBC	Chemical SP
Aliphatic polyester of dicarboxylic acid	PM632	BASF
Polyester of dicarboxylic acid	PM652	BASF

Table 1. Type, abbreviations and commercial name of plasticizers employed

The evolution of the viscosity during the beginning of the gelation process was measured in a BOHLIN CS50 rheometer by means of the oscillation test, using the 40 mm parallel plates accessory. The deformation amplitude was set to 0.005, the frequency 1 Hz, the gap between plates 0.7 mm and the heating rate was 10 °C/min.

An amount of 100 g of each plastisol was rotomoulded in a Cu–Ni semi spherical mould. A Rotospeed RL1-400 rotational moulding machine was employed. Except where indicated, the arm to plate rotation ratio was set to 12/4, (i. e. 12 min⁻¹/4 min⁻¹), the oven temperature was 230 °C for 8.5 min and the cooling cycle was water spray for 1 min and blow air for 1 min. All processed plastisols were degasified prior to processing, and as expected no air bubbles were observed in any rotomoulded sample; in addition, all samples did show a smooth and bright inner surface.

Fig. 2 shows a drawing of the mould used, including its measurements and thickness, as well as the rotation axis. The lid of the mould was of aluminium and the mould was of a Cu–Ni alloy typical in this type of process. Since the lid thickness was higher than that of the mould and the thermal conductivity was lower, the thickness of PVC built on it was correspondingly lower. All these are specifications of the mould, since this part has to be removed and rejected in the final product. Due to this fact, we concentrated only on the thickness distribution in the hemispherical part of the mould, and the wall thickness of the rotomoulded parts was measured at 21 different points in the hemispherical part of the piece at regular intervals as shown in Fig. 3 and the standard deviation of the wall thickness was obtained. The instrument used for thickness measurements is a micrometer of the Quickmike (range: [25 to 55 mm]; Resolution 0.001 mm and accuracy $\pm 4 \mu\text{m}$).

3 Results and Discussion

Viscosity measurements were carried out until the material reached a viscosity of 1000 Pa · s, due to the fact that at such viscosity the plastisol is not likely to flow anymore, and this

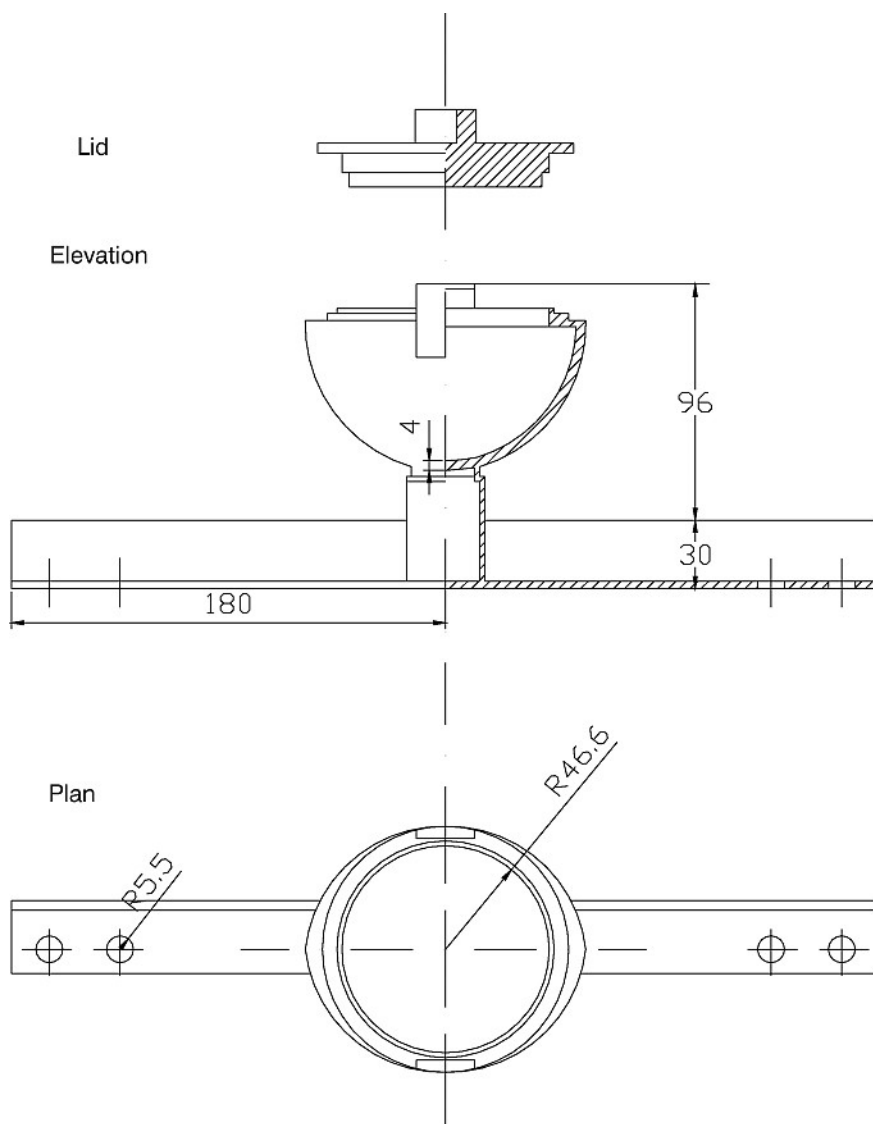


Fig. 2. Drawing of the mould all measures in mm

viscosity corresponds to a point close to the gelation point (where the viscosity increases rapidly), see Fig. 1. For instance, the calculated velocity (according to momentum balances) of such a paste flowing on a surface at 85° to the horizontal and forming a layer of 7 mm thickness will be lower than 0.02 cm/s, velocity at which the plastisol would not have time enough to flow in the mould surface.

Figs. 4 and 5 show the evolution of the logarithm viscosity with the temperature for the different PVC plastisols until a value of $1000 \text{ Pa} \cdot \text{s}$ is reached in order to better observe the changes in viscosity. As commented above, initially in all plastisols a slight decrease of the viscosity is observed as a consequence of the temperature increase. When the interactions of the plasticizer with the PVC start and the gelation process takes place, a sharp increase in viscosity is observed.

Although the process of thermosetting of a resin system is different to that of gelation of a plastisol, the distribution of PVC plastisols around the mould may take place in a similar way as in liquid thermoset systems [11 to 13], and the shape of these curves may affect the material distribution. Table 2

shows the initial viscosity, minimum viscosity and the standard deviation of part wall thickness of the mouldings. The temperature at which the viscosity of $1000 \text{ Pa} \cdot \text{s}$ is attained (i. e. the plastisol does not flow) is also shown and is referred to as the gelation temperature, T_{1000} .

The first factor that seems to affect the wall thickness distribution (Table 2) is the minimum viscosity reached by the plastisol. Plastisols with the lowest minimum viscosity (0.3 to $0.5 \text{ Pa} \cdot \text{s}$) give the rotomoulded specimens with the most uniform wall thickness. However, when comparing plastisols with the same or similar minimum viscosity (i. e., PT711, DOA and DHA, or DINP and PT911), the velocity of the gelation process, given by the slope of the curves viscosity-temperature, has the dominant effect. In this case, those plastisols with the faster gelation process (more marked viscosity changes) yielded the highest uniformity of wall thickness. The minimum viscosity attained by these plastisols is low enough to ensure a good and complete distribution of the plastisol in the mould, when gelation starts. When it has already happened, a fast gelation enhances the quality of the mouldings.

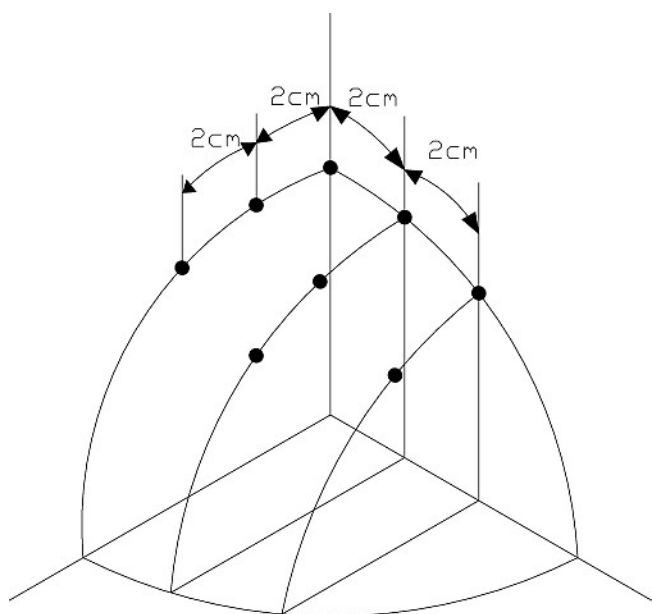


Fig. 3. Schematic distribution of points measured on a quarter of the hemispherical surface

However, if the minimum viscosity is too high a low gelation rate could allow better results, since under these conditions the plastisol has more time to be distributed uniformly in the mould.

Another factor affecting the standard deviation of part wall thickness is the gelation temperature (T_{1000}). If gelation occurs at very low temperatures, there is not time enough for the plastisols to completely cover the mould. In this case, some plastisol probably still remains in the pool when the viscosity has increased too much. This fact could explain the differences observed among DOP, DBP and DMP, where the minimum viscosity is similar, but in spite of DMP having the higher slope, it presents the worse uniformity due to its very low gelation temperature (60 °C). If the gelation temperature is too high, there can also be problems in the distribution of the material, as can be observed for DNA. In this case, a high gelation temperature associated to a low gelation rate allows the plasti-

Plasticizer	η_0 Pa · s	η_{min} Pa · s	T_{1000} °C	Standard deviation of wall thickness mm
CITR	0.6	0.4	83	0.0365
PT711	0.7	0.3	101	0.0371
DOA	0.4	0.3	100	0.0410
DHA	0.3	0.3	74	0.0418
DINP	0.9	0.5	83	0.0495
PT911	1.0	0.5	>100	0.0505
HF600	0.9	0.8	>100	0.0630
HF700	1.5	0.9	>100	0.0705
PM652	16.5	3	105	0.0728
DOP	2.1	1.1	84	0.0731
DNA	0.4	0.3	>100	0.0769
PT11	1.1	0.8	>100	0.1362
DBP	1.7	1.2	65	0.1941
PM632	12.0	3.7	85	0.1952
DMP	1.2	1.0	60	0.2046

Table 2. Initial viscosity, η_0 , minimum viscosity, η_{min} , gelation temperature, T_{1000} (°C), and standard deviation of part wall thickness for mouldings obtained at 230 °C for 8.5 min and rotation ratio of 12/4

sol layers to drop and slush provoking a bad distribution of the material.

Since most of the problems described during the distribution of the material in the mould are associated with the time the pool of material needs to be distributed on the mould walls, it is logical to assume that variables such as mould temperature, oven temperature and rotation speed could affect the behaviour of the plastisols.

Table 3 shows the standard deviation of part wall thickness for the plastisols of DOP at different plate speed, arm speed, and rotation rate. Due to the fact that it is not possible to maintain two of these variables while varying the other, the analysis is complicated. Although the arm speed does not show a clear trend on wall thickness uniformity, the plate speed has a more relevant influence, as found by Harkin-Jones [11, 14] for the case of reactive liquid polymers. When maintaining the rotation ratio, the uniformity in wall thickness increases by de-

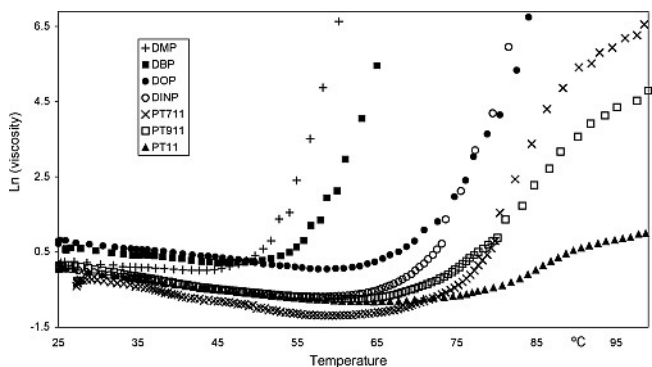


Fig. 4. Evolution of logarithm (base e) viscosity with temperature for plastisols formulated from the phthalate plasticizers. (heating rate 10 °C/min, frequency 1 Hz, shear stress 0.005, gap 0.7 mm)

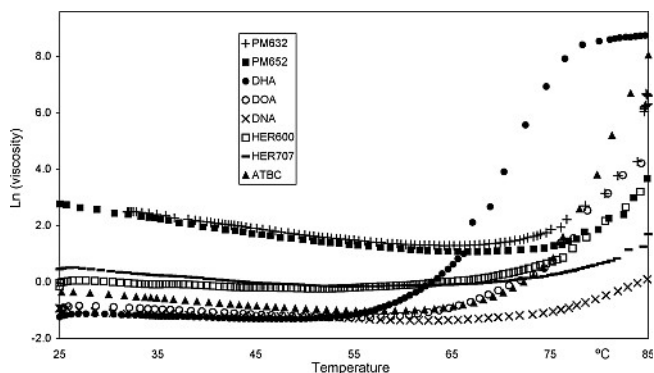


Fig. 5. Evolution of logarithm (base e) viscosity with temperature for plastisols formulated from plasticizers from adipates, ester and citrate families (heating rate 10 °C/min, frequency 1 Hz, shear stress 0.005, gap 0.7 mm)

Plate speed mm	Arm speed min ⁻¹	Rotation ratio	Standard deviation of part wall thickness mm
Effect of arm speed, plate speed constant			
12	8	1.5	0.0515
12	4	3	0.0731
12	2	6	0.0497
Effect of plate speed, arm speed constant			
20	4	5	0.0789
12	4	3	0.0731
4	4	1	0.2926
Effect of speed, rotation ratio constant			
18	6	3	0.0778
12	4	3	0.0731
6	2	3	0.0536

Table 3. Standard deviation of part wall thickness for mouldings obtained

creasing the plate speed. For example, the DOP plastisol has a relatively high minimum viscosity (Table 2) and low gelation rate; so there is a poor distribution of the material around the mould and thus, low rotation speeds are required in order to favour the uniformity of wall thickness (the liquid is lifted onto the walls slowly).

However, the effect of rotation speed was different depending on the initial viscosity, minimum viscosity and the rate at which viscosity increases during processing. Consequently, no generalization can be made, since the characteristics of each material have to be taken into account.

In conclusion, it is possible to state that for those plastisols with high minimum viscosity and low gelation rate the lower the rotation speed, the better the uniformity of wall thickness is expected. On the other hand and according to other authors [11, 14], for plastisols with low minimum viscosity and fast gelation rate, a high rotation speed could enhance the process.

4 Mathematical Model for the Correlation of the Rheological Data

Rheological behaviour of a plastisol is a consequence of the characteristics of PVC and the plasticizer employed [6 to 10]. As shown above, the knowledge of the shape of the curves in Figs. 1, 4 and 5 is of great importance for the prediction of the behaviour and distribution of the material in the mould during the rotational moulding process. The main difference between plastisols in Fig. 4 is the length of the plasticizer chain (and thus the polarity), since all plasticizers belong to the phthalate family and, consequently, the type of interactions between PVC and these plasticizers are expected to be of the same nature.

As stated in the introduction, the viscosity of this type of system during the first stage of gelation depends on the volumetric fraction of the discontinuous phase, the molecular weight of the continuous phase and the temperature. Thus, we have con-

sidered these two effects: the solution of PVC in the plasticizer, and the swelling of the PVC by the plasticizer. In addition, we have considered the effect of the temperature on the viscosity of the continuous phase. We have also assumed some hypotheses to simplify the formulation of the model. Accordingly we have considered that the viscosity (experimental values meas-

Nomenclature

E_{ad}	activation Energy in the kinetic equation for the PVC dissolution process (kJ/mol)
E_{as}	activation Energy in the kinetic equation for the PVC swelling process (kJ/mol)
E_{av}	activation Energy in the Arrhenius equation for the temperature dependence of the viscosity (kJ/mol)
f	factor for the volumetric fraction of solids (dimensionless)
K_d	constant of the kinetic equation for the PVC dissolution process (g/s)
K_s	constant of the kinetic equation for the swelling of the PVC (g/s)
K_v	constant of the viscosity model that shows the effect of molecular weight and temperature on the plastisol viscosity ($\text{Pa} \cdot \text{s}/(\text{g}/\text{mol})^n$)
$m_{\text{plasticizer}}^c$	plasticizer mass in the continuous phase (g)
$m_{\text{plasticizer}}^d$	plasticizer mass in the discrete phase (g)
$M_{\text{plasticizer}}$	molecular weight of the plasticizer (g/mol)
m_{PVC}^c	PVC mass in the continuous phase (g)
m_{PVC}^d	PVC mass in the discrete phase (g)
M_{PVC}	average molecular weight of the resin (g/mol)
M_w	average molecular weight of the continuous phase of the plastisol (g/mol)
n	exponent of the power law viscosity model (dimensionless)
n_d	reaction order for the kinetics of the PVC dissolution (dimensionless)
n_f	exponent of the equation for the calculation of the factor for the volumetric fraction of solids (dimensionless)
n_s	reaction order for the kinetic equation of the PVC swelling process (dimensionless)
R	Ideal-Gas Law constant (kJ/(mol · K))
r	PVC dissolution velocity (g PVC _{dissolved} /s)
t	length of time since the gelation process started (s)
T	absolute temperature of the plastisol (K)
T_o	reference temperature (350 K) in the kinetic equation for the PVC dissolution process (K)
$w_{\text{plasticizer}}^c$	mass fraction of the plasticizer in the continuous phase ($\text{g}_{\text{plasticizer}}/\text{g}_{\text{continuous phase}}$)
w_{PVC}^c	mass fraction of the PVC in the continuous phase ($\text{g}_{\text{PVC}_{\text{dissolved}}}/\text{g}_{\text{continuous phase}}$)
ϕ	current volumetric fraction of solids ($m_{\text{solids}}^3/m_{\text{total}}^3$)
ϕ_s	maximum volumetric fraction of solids ($m_{\text{solids}}^3/m_{\text{total}}^3$)
η	viscosity of the plastisol ($\text{Pa} \cdot \text{s}$)
η_r	relative viscosity which is defined as actual viscosity divided by the viscosity at 37 °C

ured at 1 Hz) of the system can be represented by the following equation:

$$\eta = K_v (M_w)^n e^{\frac{E_{av}}{R}(\frac{1}{T} - \frac{1}{T_o})} f, \quad (1)$$

that corresponds to the viscosity of a suspension with the viscosity of the continuous phase that depends of its molecular weight (i. e. $K_v (M_w)^n$) and is corrected by the temperature effect (i. e. $e^{\frac{E_{av}}{R}(\frac{1}{T} - \frac{1}{T_o})}$) and by the suspension of solids (i. e. factor f), and where K_v is the constant of the power law viscosity model used, M_w is the average mass molecular weight, n is the power of M_w , E_{av} is the activation energy in the Arrhenius dependence of η with T , T_o is a temperature of reference (350 K).

In this Eq. 1 there are two terms to be better defined: f and M_w . The factor for the volumetric fraction of solids (f) is evaluated by the next expression:

$$f = (1 - \phi / \phi_s)^{-n_f}, \quad (2)$$

where ϕ is the current volumetric fraction of solids and ϕ_s is the maximum volumetric fraction of solids which is 0.65 for spherical particles.

M_w represents the average mass molecular weight of the continuous phase and can be calculated as follows:

$$\begin{aligned} M_w &= M_{PVC} w_{PVC}^c + M_{plasticizer} w_{plasticizer}^c \\ &= M_{PVC} w_{PVC}^c + M_{plasticizer} (1 - w_{PVC}^c), \end{aligned} \quad (3)$$

where w_{PVC}^c and $w_{plasticizer}^c$ are, respectively, the mass fractions of PVC and plasticizer in the continuous phase. But w_{PVC}^c and $w_{plasticizer}^c$ are not constant, since the PVC is being solved by the plasticizer and thus, passing from the dispersed phase to the continuous phase:



We have considered that this process could be represented by a generic n -order kinetic equation:

$$\frac{dm_{PVC}^d}{dt} = -K_d e^{-\frac{E_{ad}}{R}(1/T-1/T_o)} (m_{PVC}^d)^{n_d} = -\frac{dm_{PVC}^c}{dt}, \quad (5)$$

where m_{PVC}^d is the remaining undissolved PVC. However, in the initial stages of gelation, when a low amount of PVC has been dissolved in the continuous phase, it could be reasonable to assume that the velocity of this process does not depend on the amount of PVC resin (undissolved PVC remains approximately constant); therefore, it is possible to assume a zero order reaction:

$$r = -\frac{dm_{PVC}}{dt} = K_d e^{-\frac{E_{ad}}{R}(1/T-1/T_o)}. \quad (6)$$

An attempt to correlate the data considering only these two effects, (i. e. not considering the solids fraction) is capable of correlating the results only up to viscosities of around 10 to 20 Pa · s. In order to represent the further sharp increase in viscosity, the f factor must be considered. Thus, we have included the swelling of the discrete PVC by the plasticizer that increases the volumetric fraction of solids. As a simplification, we have considered that the factor f can be calculated in terms of the mass fraction instead of the volumetric fraction. For the

penetration of the plasticizer into the structure of the PVC we also suggest a generic n order kinetic equation:



$$-\frac{dm_{plasticizer}^c}{dt} = K_s e^{-\frac{E_{as}}{R}(1/T-1/T_o)} (m_{plasticizer}^c)^{n_s}. \quad (8)$$

This model also includes the step of the gelation process where the plasticizer solvates the resin surface and, as a result, it swells the PVC particles. For calculation purposes a calculation basis of 100 g of PVC has been established.

Thus, it is possible to calculate the mass fraction of PVC in the continuous phase at any time by means of the equation:

$$m_{PVC}^c = \int_0^t K_d e^{-\frac{E_{ad}}{R}(1/T-1/T_o)} dt. \quad (9)$$

The mass of plasticizer which has penetrated into the PVC resin is calculated by integration of Eq. 7:

$$m_{plasticizer}^d = \int_0^t K_s e^{-\frac{E_{as}}{R}(1/T-1/T_o)} (m_{plasticizer}^c)^{n_s} dt. \quad (10)$$

These equations have been used for the correlation of the experimental curves of viscosity versus temperature obtained for the plasticizers of the phthalate family with different molecular weights: DMP, DBP, DOP and DINP and PT11. Plasticizers PT711 and PT911 are commercial mixtures of heptyl, nonyl, and undecyl phthalates, and their corresponding curves have not been included in the correlation.

The following objective function (O.F.) has been minimised; using the tool "solver" of the Excel spreadsheet,

$$O.F. = \sum_{i=1}^5 \frac{1}{d_i} \left\{ + [(\eta_r)_{exp} - (\eta_r)_{cal}]^2 \right\}, \quad (11)$$

where η_r is the relative viscosity, i. e. actual viscosity divided by the viscosity at 37 °C, and d_i is the number of values of the experimental viscosity considered for the i plasticizer.

In order to reduce the number of parameters of the model the value of K_v for each plasticizer has been obtained from the E_{av} parameter and the initial values (at 37 °C) of the experimental viscosity and the volumetric fraction of solids, as:

$$K_v = \frac{\eta_r(37^\circ C)}{(M_{plasticizer})^n e^{E_{av}/R(37+273)} f(37^\circ C)}. \quad (12)$$

Also, the same values of the reaction orders n and n_s , ϕ_s and n_f have been assumed for all plasticizers to minimised the objective function. As a result, the independent parameters for each plasticizer are only 5: E_{av} , K_d , E_{ad} , K_s and E_{as} . Fig. 6 shows a sketch of the calculus process followed in the Excel spreadsheet.

Fig. 7 shows the result of the correlation obtained and Table 4 contains the value for the common and the individual parameters of the model proposed. Owing to the wide range of the viscosity variation, up to 1000 Pa · s, Fig. 7 shows the logarithm of the relative viscosity. In this way it is feasible to observe the correlation with clarity for all the values of the plastisol viscosity. A good fitting for the complete curve of the viscosity versus temperature is obtained for all of the plasti-

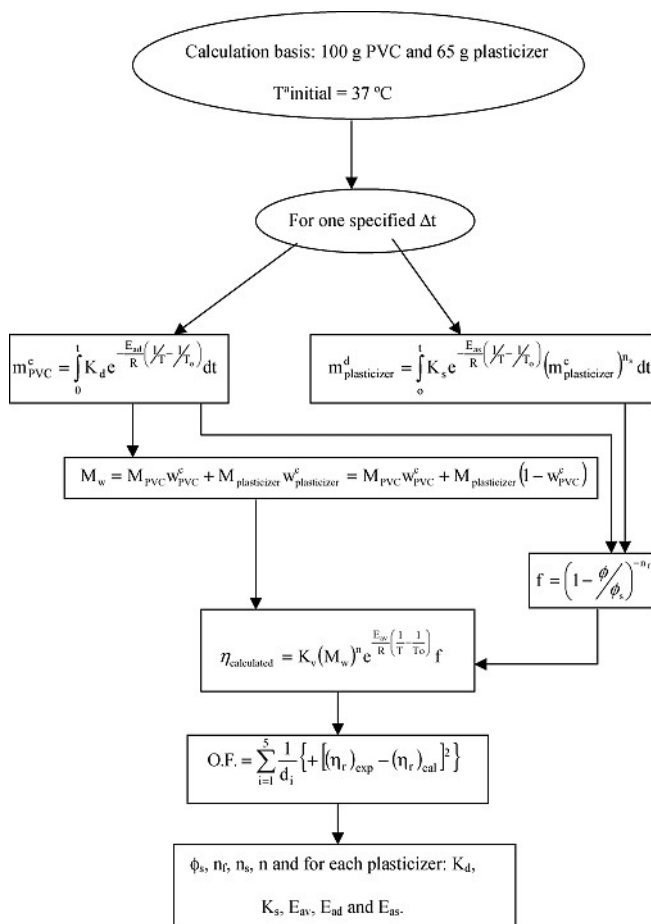


Fig. 6. Computational scheme

cizer studied (Fig. 7). Fig. 8 enlarges the viscosity curve (without logarithm) to show the performance of the model at lower viscosities.

There is a trend between the kinetic constants and the molecular weight of the plasticizer, which is proof of the suitability of the model proposed. As can be observed in Fig. 9, the higher the molecular weight of the plasticizer, the lower the values of the kinetic constant for the PVC dissolution (K_d) and the kinetic constant for the swelling of the PVC (K_s). In addition, the activation energy of the kinetic equations used in the model (E_{as} , E_{ad} and E_{av}) exhibits some trend with the molecular weight of the plasticizer (Fig. 10). While the activation energies of the dissolution and swelling processes decrease with a

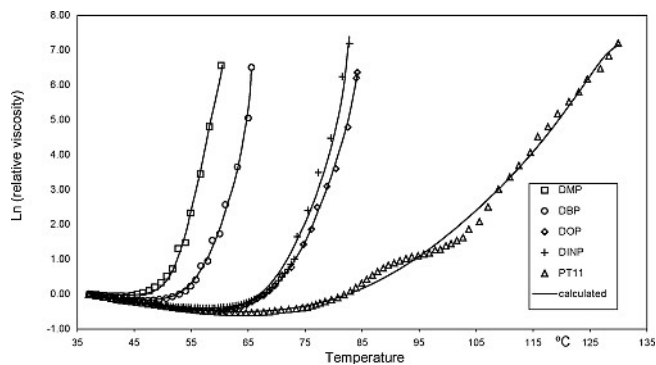


Fig. 7. Evolution of logarithm (base e) relative viscosity vs temperature predicted by the model for plastisols of DMP, DBP, DOP, DINP and PT11

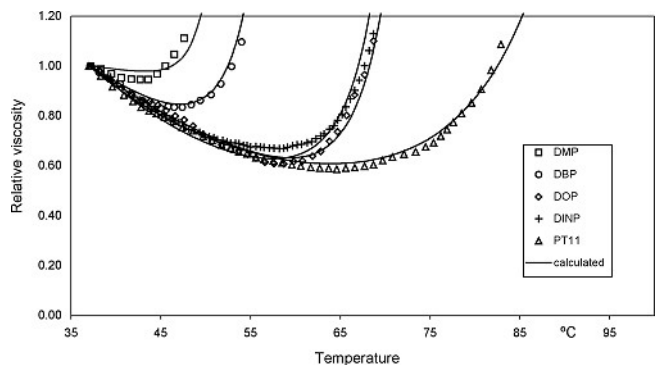


Fig. 8. Enlargement at lower viscosities of the curve of relative viscosity vs temperature predicted by the model for plastisols of DMP, DBP, DOP, DINP and PT11

plasticizer of higher molecular weight, the activation energy of the temperature dependence of the viscosity increase.

The study of the proposed model allows some trends to be established between the parameters of the model and the shape of the viscosity curve. An increase in the value of K_d causes a displacement to lower temperatures at the onset of gelation. The onset value of the activation energy in the kinetic equation affects the curve in the same way as K_d does; the higher the value of E_{ad} , the higher the magnitude of the left displacement of the curve.

The parameter which establishes the dependence between viscosity and the temperature, E_{av} , strongly affects the minimum relative viscosity. The higher the value of this parameter,

Plasticizer	n	E _{av} kJ/mol	K _d g/s	E _{ad} kJ/mol	K _s g/s	E _{as} kJ/mol	n _s	φ _s	n _f
DMP	1.85	3.79	2.57E + 03	476	2.47E + 01	350	0	0.65	1.00
DBP		19.12	2.91E + 00	279	9.10E + 00	219			
DOP		21.00	4.60E - 02	240	1.60E - 01	200			
DINP		31.66	3.51E - 02	230	1.41E - 01	50			
PT11		33.18	1.59E - 03	85	3.86E - 02	5			

Table 4. Calculated values of the parameters of the model proposed

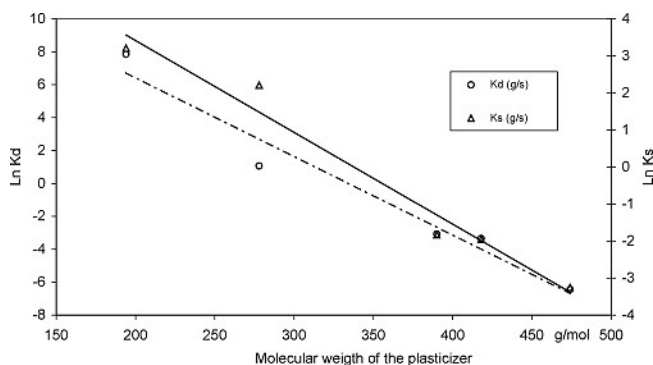


Fig. 9. Kinetic constant for the PVC dissolution (K_d) and kinetic constant for the swelling of the PVC (K_s) versus the molecular weight of the plasticizer

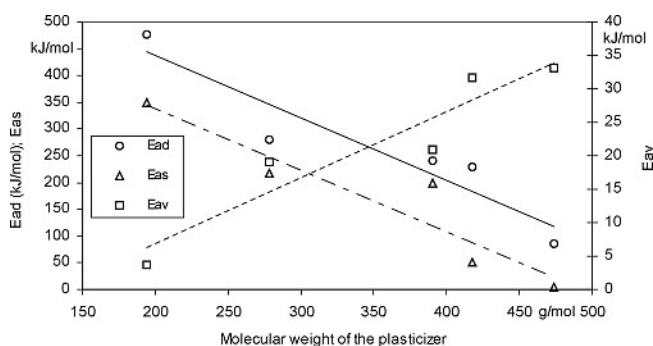


Fig. 10. Activation Energy for the PVC dissolution process (E_{ad}), for the PVC swelling process (E_{as}) and for the temperature dependence of the viscosity (E_{av}) versus the molecular weight of the plasticizer

the lower the minimum of the curve. The constant of the viscosity model, K_v , does not show any effect on the relative viscosity curve. This parameter only affects the values of the absolute viscosity.

5 Conclusions

Plastisol distribution in the mould during the rotational moulding process is strongly affected by minimum viscosity, rate of gelation and gelation temperature. These variables depend

mainly on the system PVC-plasticizer selected. Rotation speed also affects the material distribution. The correct combination of these variables leads to mouldings with a good distribution of the material. It is essential for the plastisol to have the necessary time to be distributed in the mould. In general, low viscosity materials are favoured by fast gelation rates and high rotation speeds. High viscosity materials produce better mouldings if gelation rate is low, gelation temperature is high and the rotation speed is low. A mathematical model for the correlation of the initial evolution of viscosity of plastisols formulated with plasticizers of the phthalate family can satisfactorily predict the minimum viscosity, the gelation rate and the gelation temperature with a single set of parameters. The capability of this model to describe the experimental data has been confirmed using a plot of the variation of the actual plastisol viscosity and the calculated one as a function of the temperature.

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