

Lubrication and slip flow during extrusion of plasticized PVC compounds in the presence of lead stabilizer

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Abstract

The main point of interest when discussing lubrication is to understand what lubricants do in a compound, particularly during processing. Among lubricants, we can find metal soaps, which are often heat stabilizers of PVC. In order to study the influence of lubricants on the flow properties, it is of particular interest to analyse the behaviour of the material at the die walls, where slip may be observed. Then, in the present paper, the lubricating ability of a lead stabilizer during extrusion of a plasticized PVC formulation was investigated through an instrumented die, which allowed us to have the apparent flow properties at the wall. Rough and smooth surfaces of the die were used in order to prevent or promote slip at the metal surface. From this method, it was possible to observe the slip phenomenon above a critical concentration, whereas the analysis of the die surface through SEM coupled energy dispersive x-ray spectroscopy shows that lead stabilizer migrates even at low concentration. So, slip occurs when the lubricant layer forms a continuous solid layer which modifies the polymer–metal interface properties. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The first studies concerning the lubrication of PVC attempted to classify these additives into two main classes, internal or external, according to their chemical structure.

Hartz [1] delineated two groups, one of which was composed primarily of metal soaps, while the other consisted of less polar components, e.g. paraffin waxes, low molecular weight polyethylenes and oils. Metal soaps, alone or in combination with additives of the second group, can delay the gelation time of the PVC. King and Noel [2] attempted to classify lubricants according to their ability to depress the glass transition temperature of PVC, which means with respect to their solvating power.

Lindler and Worschech [3] keep Hartz's classification, insisting on the role of these additives towards the polymer–metal interface, in relation to the processability of the compound.

So, the main point of interest when discussing lubrication is to understand the mechanism of the lubricant action during processing.

Rabinovitch et al. [4] analysed the lubrication mechanism

of two components, calcium stearate and a paraffin wax, through tests made with a Brabender plasticorder and an extruder (considering only the extruder power consumption).

Collins et al. [5] used capillary rheometry and showed that flow properties are mainly affected by the concentration of paraffin wax, while the characteristics of fusion may be greatly influenced by the calcium stearate.

The Brabender tests take into account the evolution of volume properties according to the lubricant nature, but they do not distinguish their ability to modify superficial properties leading to a slip phenomenon.

The slip study involves a direct measurement method of the polymer behaviour at the wall. In the case of PVC, slip has first been studied for rigid formulations. Chauffoureaux et al. [6], and Knappe and Krumböck [7] proved the efficiency of grooved dies to prevent slip at the wall, and to modify the flow curves of shear stress versus shear rate at the wall, in the case of a rigid PVC lubricated with a paraffin wax.

Chauffoureaux et al. [6] measured the velocity profile at the wall and found it to depend greatly on the paraffin wax concentration.

In the case of plasticized PVC, slip phenomenon has been

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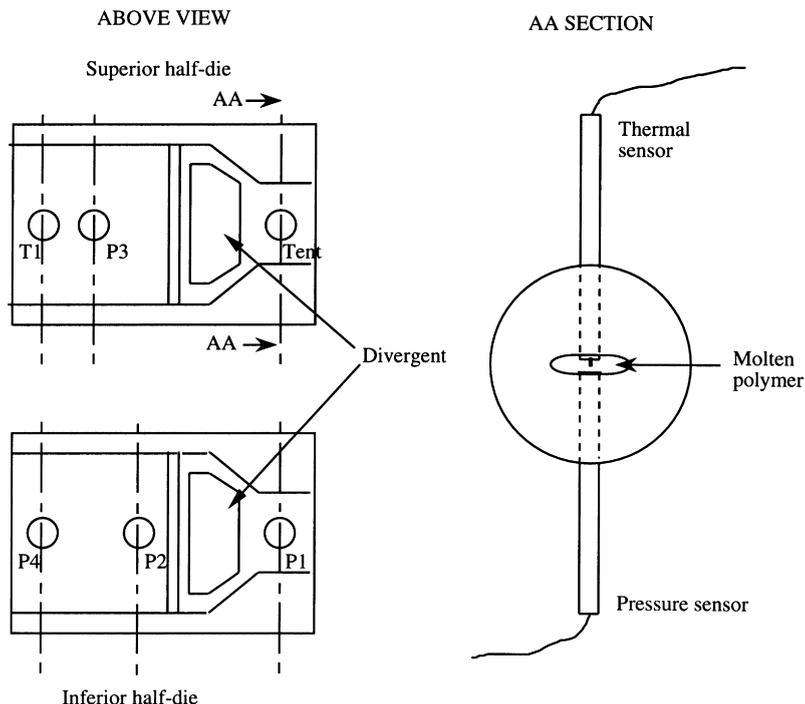


Fig. 1. Scheme of the die equipped with thermal and pressure sensors. P₁, P₂, P₃, P₄ are pressure sensors. T₁, T_{ent} are thermal sensors.

less studied. In such formulations, the rheological behaviour mainly depends on the plasticizer content, so it is more difficult to analyse small changes due to an additive in low concentration.

For example, Gonnu et al. [8] have studied the heat stabilizer behaviour of two tin stabilizers which can be distinguished in the case of rigid PVC, whereas this difference is cancelled when a diethylhexyl phthalate is added.

Aressy [9] showed that a removable die with different roughness is very helpful to detect a slip phenomenon at the wall during an extrusion process of a plasticized PVC formulation. Furthermore, a surface analysis (infra-red spectroscopy, scanning electron microscopy coupled with a x-ray diffraction probe) allowed him to detect which lubricant migrates to the wall and is responsible for the slip phenomenon.

Lead stabilizers are often known for their lubricating power. In this investigation, it is of our concern to examine the lubricating ability of a lead stabilizer by varying its concentration in a highly plasticized PVC formulation. In this aim, we analysed the flow properties of these formulations at the die wall, and the lead stabilizer migration by a chemical identification of the deposit on a die insert. Furthermore, this lead stabilizer, when used at a sufficiently high level, acts as a filler. This filler has a lamellar shape and can be oriented during the extrusion process so that the tensile properties of the material can be changed [10].

2. Slip phenomenon

When considering the occurrence of a slip phenomenon, the apparent flow properties at the wall need to be known.

A slit die was used here, and the equations leading to apparent viscosity, apparent stress and apparent shear rate can be calculated from the Navier–Stokes equations, with the commonly used hypothesis of a wall adhesion and in the case of a Newtonian fluid.

The apparent viscosity (η_{app}) was calculated according to Eq. (1):

$$\eta_{app} = \frac{\tau_{wapp}}{\dot{\gamma}_{wapp}} \tag{1}$$

τ_{wapp} is the apparent shear stress at the wall, which can be calculated according to Eq. (2), and $\dot{\gamma}_{wapp}$ is the apparent shear rate at the wall, given by Eq. (3).

$$\tau_{wapp} = \frac{\Delta P H}{2L} \tag{2}$$

$$\dot{\gamma}_{wapp} = \frac{6Q}{WH^2} \tag{3}$$

ΔP is the pressure gradient inside the die. Q is the volume flow rate, (L, W, H) are the die dimensions (length, width, height).

Table 1
Temperature profile of the different zones of the extruder Clextal BC 21

Zone	1	2	3	4	5	6	7	8
T (°C)	120	130	140	160	160	160	165	170



Fig. 2. Rough surface type.

From an experimental point of view, two types of die were used: rough and smooth, as described later in the Experimental section.

3. Experimental

3.1. Materials

A suspension PVC (Evipol SH 8020), supplied by the European Vinyl Corporation, was used. The plasticizer (Bisoflex T810T) was a nonyl trimellitate supplied by B.P. Chemicals. It was introduced at the ratio of 50 phr (weight parts per 100 weight parts of PVC resin). The heat stabilizer was a lead carboxylate (8831/E) from La Floridienne Chimie; its concentration varies from 2 to 12 phr. The notation is as follows: PVC_{Pbx} , where x is the weight parts of the lead carboxylate per 100 weight parts of PVC.

3.2. Extrusion experiments

The studied formulations were first dry-blended in a powder mixer of Papenmeier type, extruded to allow gelation of PVC and then granulated. The gelation step was achieved on a twin screw extruder (co-rotating) Clextal BC21 (length/diameter = 24). The screw speed was 550 rpm, the output was 25 kg/h. The temperature profile of the different zones of the extruder is given in Table 1. In a second step, these granules were extruded with a double-screw (counter-rotating) Leitztritz LSM 30-34, equipped with a die, as shown in Fig. 1, where the thermal and pressure sensor positions can be seen. The pressure sensors (P2, P3, P4) allow us to determine the gradient pressure inside the die, and the thermal sensor (Tent) gives the bulk temperature.

Dies with two different surface states were used:

1. a rough surface obtained by electroerosion. The scheme is shown in Fig. 2.
2. a smooth surface obtained after different steps of polishing ranging from 15 to 3 mm.

These dies were cleaned in an oven at 600°C for several hours and then removed from dust with compressed air for the rough surface, and with a 3 mm polishing solution for the smooth surface.

The temperature is set at 175°C for each zone of the extruder.

The screw rotation speed of the extruder is 100 rpm, the

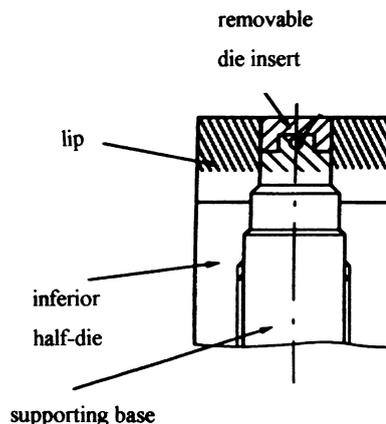


Fig. 3. Assembly of the die sample.

output is 10 kg/h and the dimensions of the slit die were: $50 \times 50 \times 1 \text{ mm}^3$, the apparent shear rate at the wall $\dot{\gamma}_{\text{wapp}}$ is 235 s^{-1} .

3.3. Surface analysis

Just before the beginning of an extrusion, a part of the smooth die is mounted on a support, e.g. a pressure sensor (explanation in Fig. 3).

This sample is then submitted to scanning electron microscopy coupled with x-ray microprobe [CAMECA of CAMEBAX type; the detector is KEVEX energy selective, Si(Li) with a window for low elements. The accelerating voltage is 25 kV and the electronic intensity is 0.7 nA].

3.4. Chlorides coulometric titration

This technique, previously described by Van Hoang and Guyot [11], is used here to assess the consumption of the stabilizer during extrusion.

The coulometer comprises two electrodes:

1. an electrode generating the Ag^+ cations, made of a platinum cathode and silver anode;
2. a detector electrode composed of a string of platinum and silver.

The titration is made by amperometry. The detector electrode records the current variation according to the generation of silver chloride.

4. Results and discussion

4.1. Influence of the lead stabilizer on PVC gelation

These experiments were made with a Haake plasticorder equipped with an internal mixer of RHEOMIX 600 type.

Sixty grams of the dry-blend are introduced into the mixer and typical curves which can be recorded are given in Fig. 4. At a temperature of 180°C (curve A), the gelation

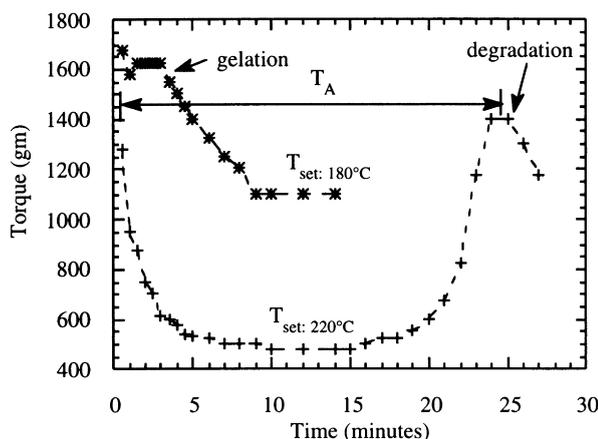


Fig. 4. Brabender test of PVC_{Pb3}, recorded at 180°C (curve A) and 220°C (curve B), rotation speed: 50 rpm. The symbols used are (■) for the torque and (▲) for the temperature.

is nearly instantaneous. When most of the stabilizer has been consumed, the torque increases, owing to crosslink formation, as shown in curve B. The time T_A between the gelation peak and crosslink peak is defined as the action time of the stabilizer system [12].

When the temperature is set at 180°C and rotation speed at 50 rpm, we can observe the influence of the lead stabilizer on gelation.

A higher lead stabilizer concentration in the formulation causes an increase at the beginning of gelation time and in the gelation temperature, as shown in Table 2 and already noticed by Kulas and Thorshaug [13] and Nagy et al. [14] in the case of a PVC stabilized with a lead stearate, whereas it does not modify the equilibrium conditions (torque and temperature).

This result is also in good agreement with dynamic mechanical measurements shown in Fig. 5. This analysis has been done with a dynamic mechanical spectrometer RMS 800, where samples with a disc shape (diameter: 25 mm, thickness: 1 mm) are put between two rough plates. The complex viscosity does not depend on the lead stabilizer concentration.

So, these results suggest that the lead carboxylates act as an external lubricant.

When the set temperature is 220°C (rotation speed: 50 rpm), we can evaluate the action time of the formulations. Increasing the lead stabilizer concentration greatly contributes to an enhancement of the action time of the stabilizer (T_A) and the residual thermal stability time (ST_r) measured at a fixed temperature and static conditions

Table 2

Time and temperature of the gelation beginning: effect of a lead stabilizer concentration variation

	PVC _{Pb3}	PVC _{Pb6}	PVC _{Pb9}	PVC _{Pb12}
Time (min)	1–2	1.25–2.75	2–4	2.5–4.5
T (°C)	165–175	165–175	175–185	175–185

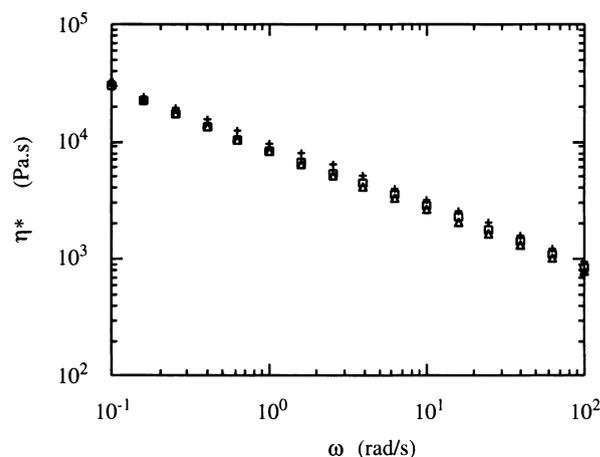


Fig. 5. Variation of complex viscosity with frequency at 203°C for: (□) PVC_{Pb4}, (Δ) PVC_{Pb8}, (+) PVC_{Pb12}.

(200°C, here and under nitrogen). The corresponding values are given in Table 3.

So, this lead soap solid at the extrusion temperature may be able to migrate near the metal surfaces and reduce the friction of polymer–metal. However, Brabender tests take into account the volume properties as well as friction at walls. Then, in order to analyse slip phenomenon during processing, experiments were performed in an extruder equipped with an instrumented die.

4.2. Influence of lead stabilizer on apparent viscosity

First, we checked that the pressure variation is linear with the distance along the die length, as shown in Fig. 6.

We can deduce from Figs 7 and 8 that the time for the two formulations (PVC_{Pb4} and PVC_{Pb12}) to reach an equilibrium is the same (about 5 min), so the values of apparent viscosity which are given in the following are taken after about 10 min of extrusion (equilibrium conditions).

The variation of viscosity with roughness of the surface and amount of lead stabilizer is plotted in Fig. 9, where the values of temperature are also reported.

Temperature decreases with an increase in lead stabilizer concentration, whereas the apparent viscosity follows the opposite tendency whatever the roughness of the die surface. The temperature measured here does not depend on slip phenomenon but reveals that this stabilizer has the power to reduce self-heating of PVC under shearing. This tendency is well-correlated to the coulometric titration of chloride ions, as shown in Table 4. Lower chloride ions are

Table 3

Action time of lead stabilizer (T_A) at 220°C (50 rpm) in the Brabender plastocorder and residual heat stability (ST_r) measured at 200°C under nitrogen

	PVC _{Pb3}	PVC _{Pb6}	PVC _{Pb9}	PVC _{Pb12}
T_A (min)	25	40	50	65
ST_r (min)	150	280	370	> 480

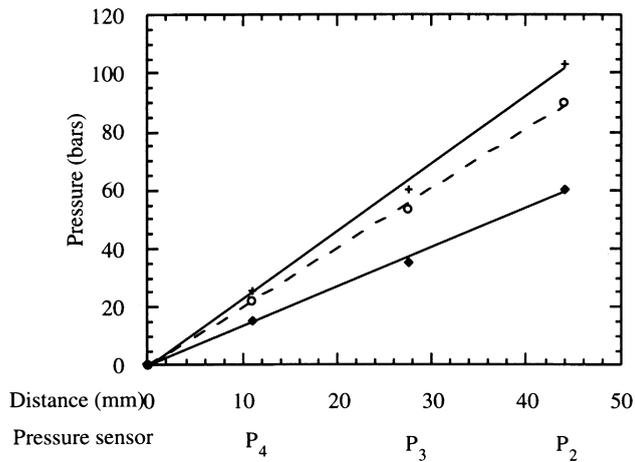


Fig. 6. Evolution of pressure along the die length for a smooth surface. (+) PVC_{Pb4}, (o) PVC_{Pb8}, (♦) PVC_{Pb12}.

generated when increasing the lead stabilizer concentration. This observation tends to reveal that this lead stabilizer, even in the solid state, reduces frictions inside the material so that the overheating and global thermal degradation of PVC during extrusion are reduced.

Furthermore, apparent viscosity substantially drops when the die surface is smooth and when the lead salt concentration is 12 phr, while it is constant during extrusion with rough die.

This fact suggests that a slip phenomenon occurs at a lead salt concentration between 8 and 12 phr. Chauffoureaux et al. [6], Knappe et al. [7], and Aressy [9] have already observed such a difference in flow behaviour with the die surface roughness.

A rough surface is indeed able to prevent lubricant from flowing because it is trapped inside the indentations.

So, a rough surface can delay a slip phenomenon to higher shear rates.

In these formulations, a minimum concentration of lead stabilizer (between 8 and 12 phr) is required to allow the PVC to slip on the metal walls. Generally, lower

Table 4

Chlorides coulometric titration after extrusion: effect of lead stabilizer concentration

	PVC _{Pb4}	PVC _{Pb8}	PVC _{Pb12}
Moles Cl ⁻ /g PVC	$(10 \pm 1) 10^{-6}$	$(8.5 \pm 0.5) 10^{-6}$	$(7.5 \pm 0.5) 10^{-6}$

concentrations of lubricant are required to induce such a phenomenon. For instance, Chauffoureaux et al. [6] showed in a rigid PVC that slip occurred for a paraffin wax concentration as low as 0.2 phr (extrusion conditions: 190°C, 50 s⁻¹). However, the rheological properties in the two cases are very different because of the presence of the plasticizer and molten temperature. In our case, the temperature is close to that of the 'gel-liquid' transition, whereas PVC is actually in a gel state at 190°C, in the study of Chauffoureaux et al.

The decrease in apparent viscosity is not an intrinsic effect of lead salt up to a critical concentration, but really a surface phenomenon, suggesting that the lead stabilizer tends to migrate from the inner to the surface layer of the material.

4.3. Analysis of the slip phenomenon mechanism

In the slip studies of PVC formulations, few authors couple their slip data with surface analysis of the die walls or the polymer itself.

Brion and Mavel [15] have shown by ESCA a high lead concentration in a 50-Å-thick layer at the surface of an extruded rigid PVC, suggesting that the lead component tends to migrate towards the surface of the material.

Aressy [9] studied the migration of the lubricant or heat stabilizer from a plasticized PVC formulation during extrusion towards the die with a die insert analysed with SEM coupled with IR spectroscopy and x-ray diffraction.

If little has been done on the analysis of slip phenomenon in the field of PVC, more attention has already been paid to polyethylenes with fluoropolymers as slipping agents.

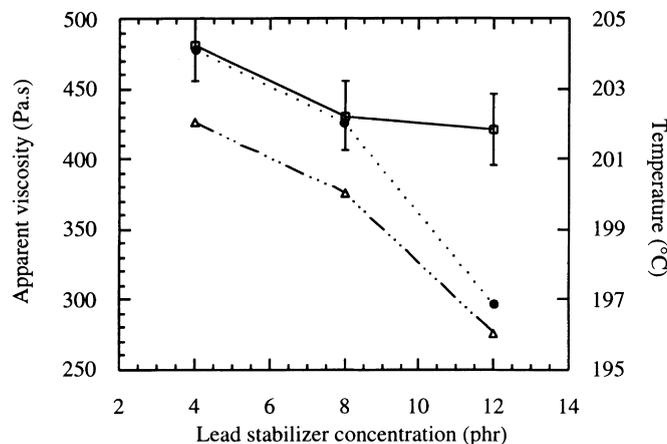


Fig. 7. Variation of viscosity and temperature with the surface type and lead stabilizer concentration. (- - -) represents apparent viscosity in the case of rough surface, (- · -) is used for apparent viscosity in the case of smooth surface, and (-Δ-) is the temperature symbol.

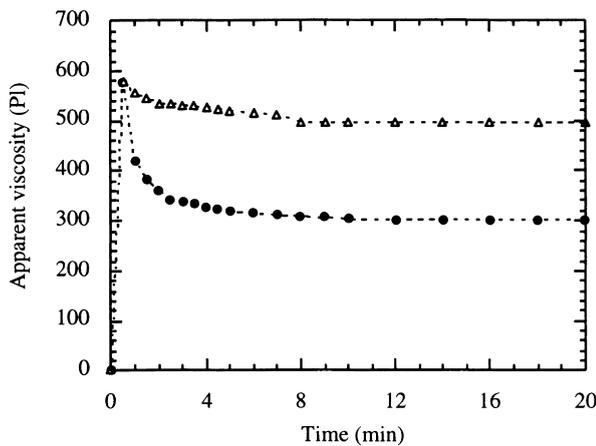


Fig. 8. Variation of apparent viscosity with extrusion time for (-Δ-) PVC_{Pb4} and (-●-) PVC_{Pb12} (smooth surface).

Two types of slip phenomena are generally admitted:

1. either the additive migrates adhere strongly to the metal walls, entailing a surface modification, onto which the polymer can slip. Above a critical concentration, an increase in slipping agent concentration does not enhance slip. This coating layer may be removed after only several hours of extrusion with a reference formulation containing no slipping agent. More details can be found in Ramamurthy [16], and Priester and Stewart [17].
2. either the additive migrates towards the metal and modifies the extreme layer of the polymer in contact with the metal surfaces. So, a lubricant layer of low viscosity can be formed promoting slip rather than a sticking contact. In that case, the lubricant layer coating the walls can be easily removed after a few minutes of extrusion, as explained by Chan et al. [18], who studied the flow properties of polyetheretherketone in which little amounts of polytetrafluoroethylene were added.

So, in this work we tried to estimate the time required for a low lead-stabilized formulation to recover its apparent

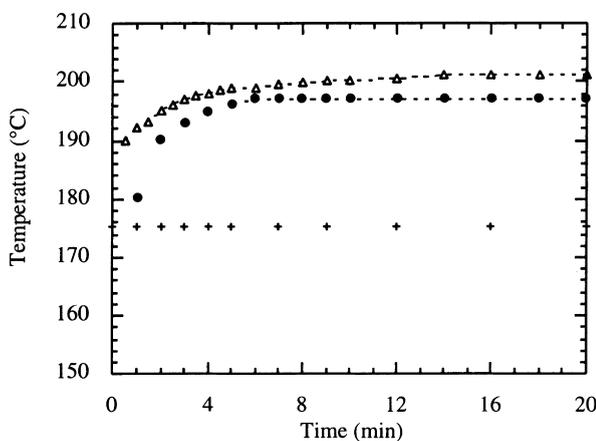


Fig. 9. Variation of temperature with extrusion time for (-Δ-) PVC_{Pb4} and (-●-) PVC_{Pb12} (smooth surface).

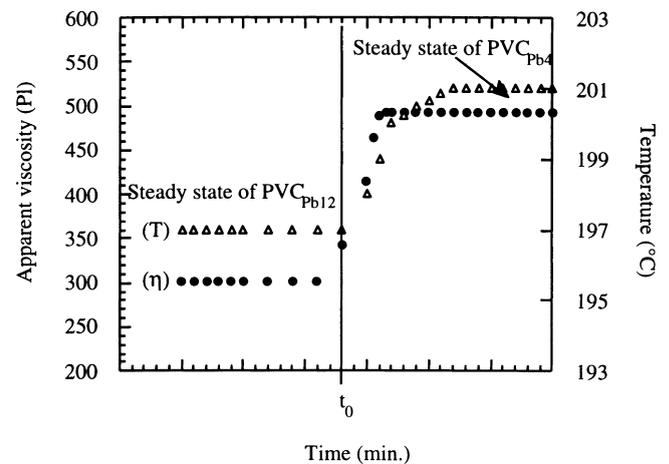


Fig. 10. Variation of (●) apparent viscosity and (Δ) temperature for PVC_{Pb12} and PVC_{Pb4} extruded successively (smooth die).

viscosity and temperature when extruded after a formulation generating slip at the die walls. When the steady state is established for a formulation (PVC_{Pb12}) flowing with a slip phenomenon, the formulation PVC_{Pb4} that does not induce a slip phenomenon is charged at the inlet of the extruder at time t_0 . As shown in Fig. 10, the apparent viscosity increases rapidly at t_0 to reach a plateau. This fact means that the lead stabilizer does not adhere strongly to the walls or the screw of the extruder, but the migration of the lead stabilizer modifies the polymer–metal interface so that a

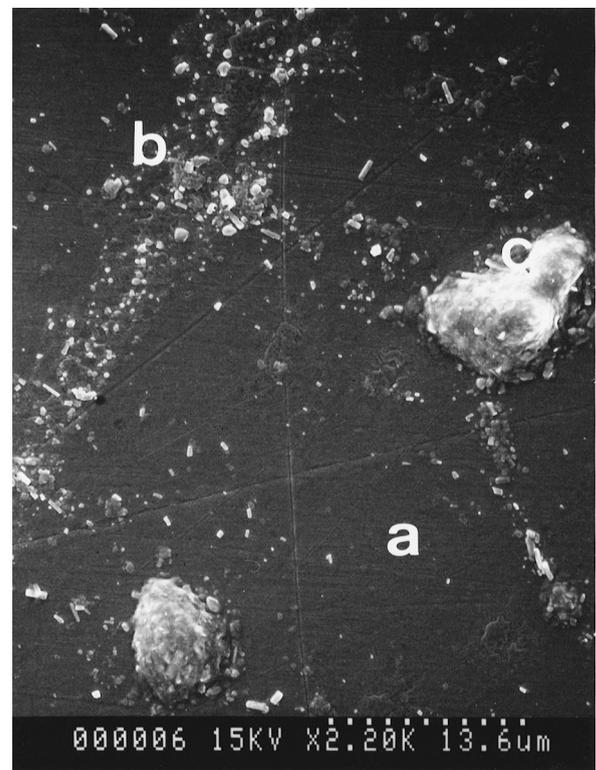


Fig. 11. SEM photo of a die sample from extrusion of PVC_{Pb12} at 196°C, $\dot{\gamma} = 235 \text{ s}^{-1}$; accelerating voltage = 15 kV, zoom = 2200.

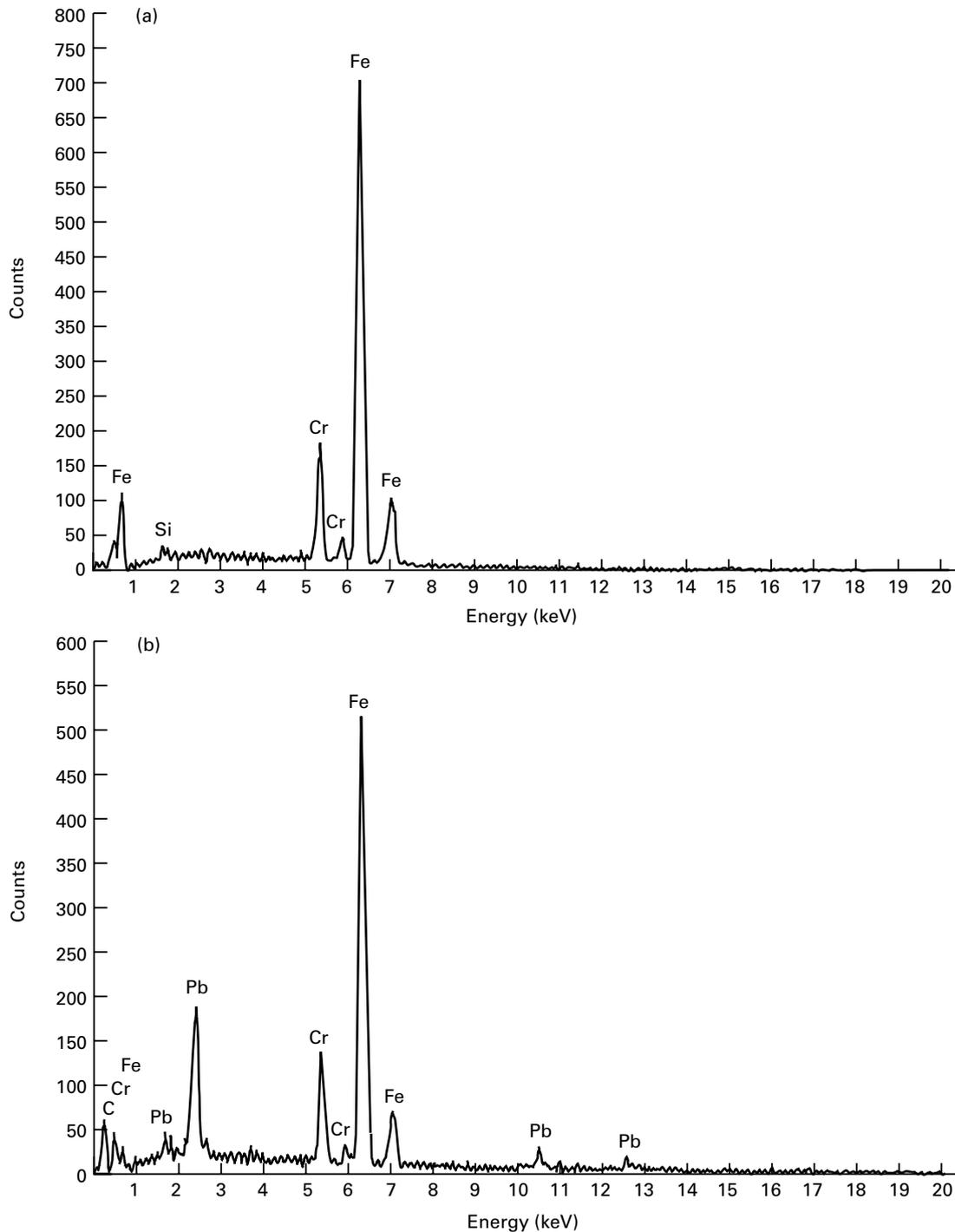


Fig. 12 a,b. X-ray pattern of zones a, b and c seen in Fig. 11.

slip phenomenon can occur. The migration of solid particles during extrusion has already been observed for polytetrafluoroethylene submitted to a surface treatment [19].

The evidence of lead stabilizer migration is confirmed by the chemical analysis of the die insert through SEM coupled with energy dispersive x-ray spectroscopy for the formulation with 12 phr of the lead component. A SEM

photo of the die surface is shown in Fig. 11, and shows three zones without the presence of chlorine atoms but with different lead compositions, as shown by x-ray patterns (Fig. 12). In zone a where agglomerates are not observed by eye, the x-ray pattern (Fig. 12a) does not show the presence of lead and carbon. In zones b and c where agglomerates are observed, the x-ray patterns (Fig. 12b and c) show the presence of lead and carbon whatever the size of the

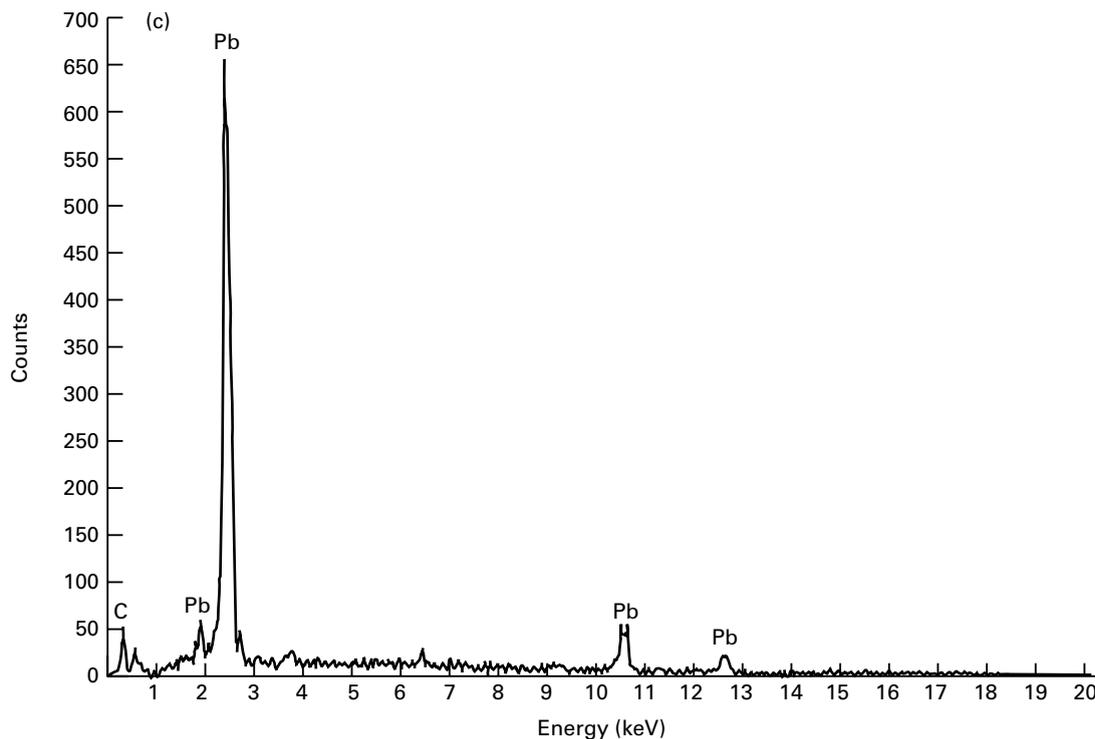


Fig. 12c. X-ray pattern of zones a, b and c seen in Fig. 11.

agglomerates. When the lead stabilizer is used at high concentration (12 phr), this study proves that only lead carboxylate is observed on the surface of the die walls and does not constitute a continuous solid film.

When extruding a formulation with a lower lead stabilizer

concentration (2 phr, PVC_{Pb2}), lead and carbon are together present on the metal surface as shown by the x-ray pattern (Fig. 13). These two elements prove that lead carboxylate migrates towards metal even at low concentration. The x-ray pattern also shows the presence of chlorine atoms,

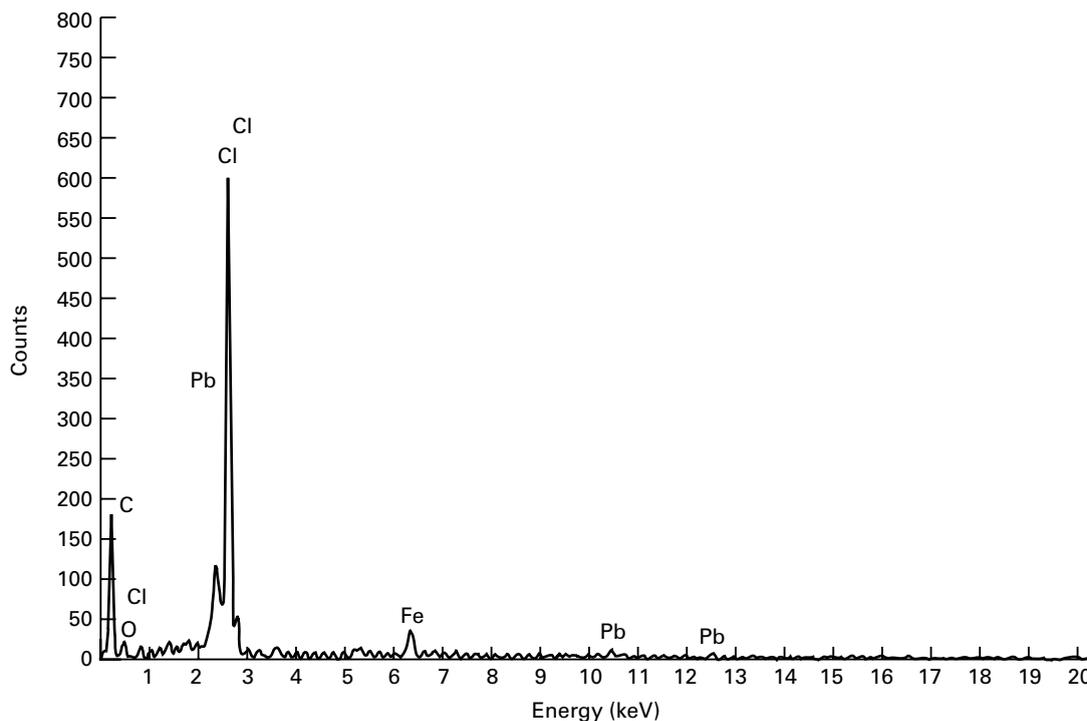


Fig. 13. X-ray pattern of a die sample coming from the extrusion of PVC_{Pb2} .

this proves that PVC adheres to the die surface when the concentration of the lead stabilizer is not enough high.

All these results suggest that a thin layer of lead stabilizer is formed at the surface of the PVC material, and constitutes an interface between the metal surface of the die and polymer. Then, the continuity and thickness of this lubricating layer depend on the concentration of the lead carboxylate. Because the slip appears above 8 phr of lead salt, it is possible to conclude that the continuity of this lubricating layer occurs from this concentration, and its thickness might be several tens of angstroms [15]. This lubricated layer reduces the friction at the die walls and the polymer can slip when it constitutes a continuous layer. Furthermore, stabilizer migration does not depend on time but on concentration.

5. Conclusion

In this study, we demonstrated the lubricant role of a lead carboxylate used as a heat stabilizer by studying its ability to delay fusion time of PVC and induce a slip phenomenon at the die walls of an extruder. Rough and smooth surfaces of the die were used to promote or prevent slip. Slip occurs above a critical concentration (8 phr), although its presence on the die surface was detected for lower concentrated formulations. So, slip occurs when the lubricant layer constituted by the lead component after migration forms a continuous solid layer which modifies the polymer–metal interface properties.

Surface analyses and the slip phenomenon study show that this lead carboxylate has an external lubricant power. Moreover, coulometric titration of chloride ions shows that the chloride accumulation is reduced when slip occurs, suggesting that the overheating of the material is decreased, which may also be due to an internal lubricant power of this heat stabilizer.

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