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Calcium Stearate–Stearic Acid as Lubricants for Rigid Poly(vinyl Chloride) (PVC). Capillary Rheometer Measurements and Extrusion Properties

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Synopsis

Capillary rheometer measurements show that stearic acid can be characterized as a normal lubricant. If the content of stearic acid is increased in rigid PVC formulations, the melt viscosity will decrease. This leads to a corresponding increase of shear rate and volumetric flow rate. The influence of calcium stearate is opposite to the normal characteristic of a lubricant. Increasing amounts of calcium stearate lead to an increased melt viscosity and a decreased shear rate and volumetric flow rate. In the extrusion of rigid PVC, the apparent "lubricating" effect of calcium stearate is probably due to the increased friction with resulting heat evolution and higher mass temperature, leading to a decreased viscosity of the plastic melt. This is in agreement with the results of the extrusion experiments. Both mass temperature and power consumption decrease when stearic acid is added and increase when calcium stearate is added to the formulation.

Introduction

The extrusion of rigid poly(vinyl chloride) (PVC) pipes or tubing from dry blend with twin screw extruders is of increasing importance in the plastics processing industry. The lubricant combination calcium stearate–stearic acid is very common for such formulations.

This paper describes work done to determine the effect of lubricant addition and processing temperature on flow behavior of rigid PVC. The flow properties of the PVC were characterized by the polymers performance in a high-pressure capillary rheometer.

Some of the more interesting formulations, according to results of the the rheometer analysis, were selected for extrusion experiments.

Materials

The following PVC formulations were studied: Norvinyl S-2-65, 100 parts; Tribase (tribasic lead sulfate), 1.6 parts; DS 207 (dibasic lead stearate), 1.2 parts; Omya BSH (calcium carbonate), 1.0 parts; stearic acid, varied in the range 0–1 parts; calcium stearate, varied in the range 0–1 parts.

The sheets were processed on a laboratory calendar for 5 min and cut into small pieces. These were preheated in a constant temperature cabinet at 160°C for 20 min prior to charging the rheometer. Dry blend and granulate were used for the corresponding extrusion experiments.

Equipment

The rheometer used is a high-pressure capillary viscometer, type Goettfert HK 1000/1600. It is shown schematically in Figure 1. The instrument consists of an electrically heated metal cylinder and a piston driven by a hydraulic system with a maximum force of 1000 kp. It is equipped with a temperature controller and recorders for pressure and temperature. The capillary has a circular cross section and a length-to-diameter ratio of 20/1. Volumetric flow rates were calculated from the weight of the extruded samples by use of specific volume data measured with a dilatometer.

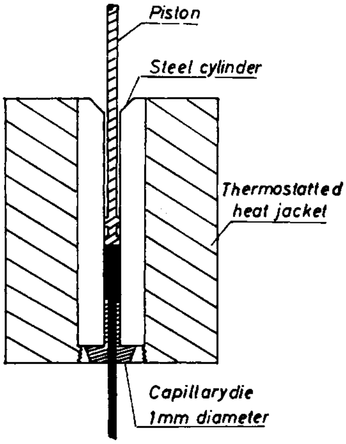


Figure 1.

A 30 mm Troester machine with a single 20 D screw (compression ratio 3.2:1) was used for the extrusion experiments. The extruder was equipped with a $^3/_4$ in. annulus die. Output, melt temperature, back pressure, and power consumption were recorded.

Experimental Design

Table I shows the experimental design procedure[1] used for the rheometer analysis. It consists of three blocks with a total of 20 single trials. In the present case each single result represents a mean value of two measurements.

The variables in Table I appear as coded quantities. The relationship between coded and real values is shown in Table II. X_1, X_2, and X_3 represent the amount of calcium stearate, stearic acid, and melt temperature, respectively.

The functional relationship between the rheological data (volumetric flow rate, shear rate, and apparent viscosity) and the independent variables were determined by regression analysis on a Univac 1107 computer. A quadratic model was used. Curves shown in Figures 2–8 are based on values obtained by solving the functions.

TABLE I

X_1	X_2	X_3
−1.000	−1.000	1.000
1.000	−1.000	−1.000
−1.000	1.000	−1.000
1.000	1.000	1.000
0.000	0.000	0.000
0.000	0.000	0.000
−1.000	−1.000	−1.000
1.000	−1.000	1.000
−1.000	1.000	1.000
1.000	1.000	−1.000
0.000	0.000	0.000
0.000	0.000	0.000
−1.633	0.000	0.000
1.633	0.000	0.000
0.000	−1.633	0.000
0.000	1.633	0.000
0.000	0.000	−1.633
0.000	0.000	1.633
0.000	0.000	0.000
0.000	0.000	0.000

TABLE II

Coded values	X_1 Ca stearate, parts per hundred parts polymer	X_2 stearic acid, parts per hundred parts polymer	X_3 Temperature, °C
−1.633	0.000	0.000	180
−1.000	0.194	0.194	182
0.000	0.500	0.500	185
1.000	0.806	0.806	188
1.633	1.000	1.000	190

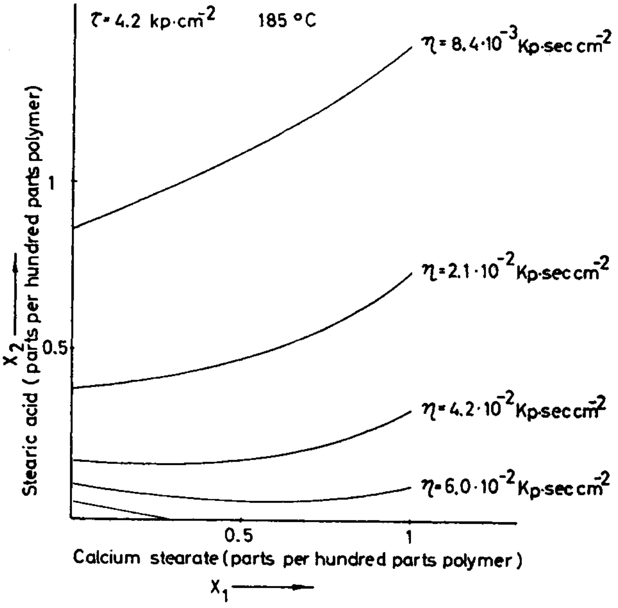


Figure 2.

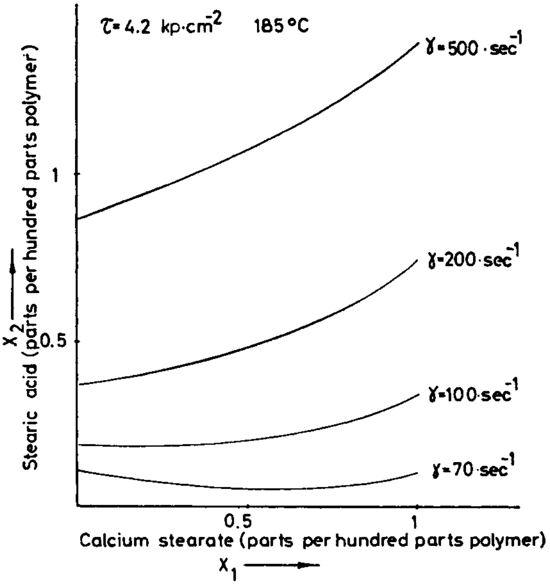
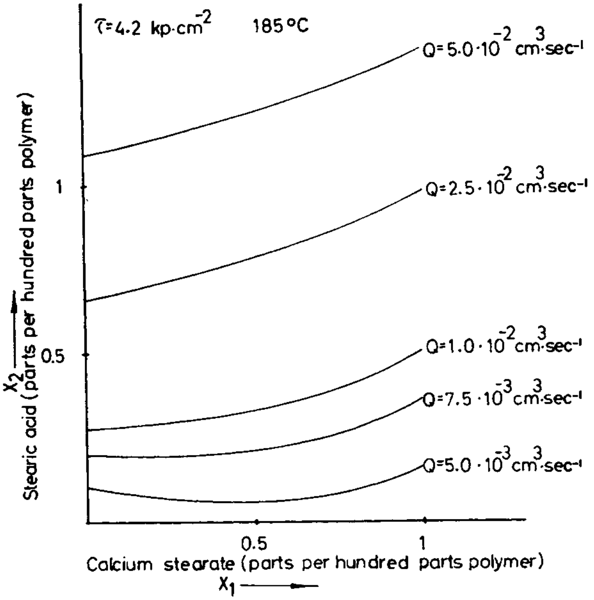


Figure 3.



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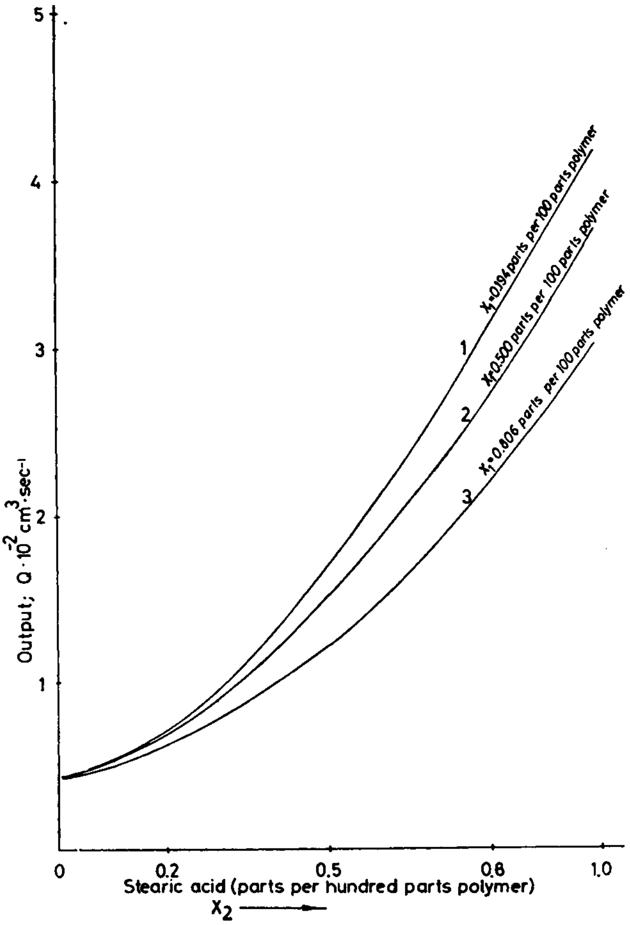

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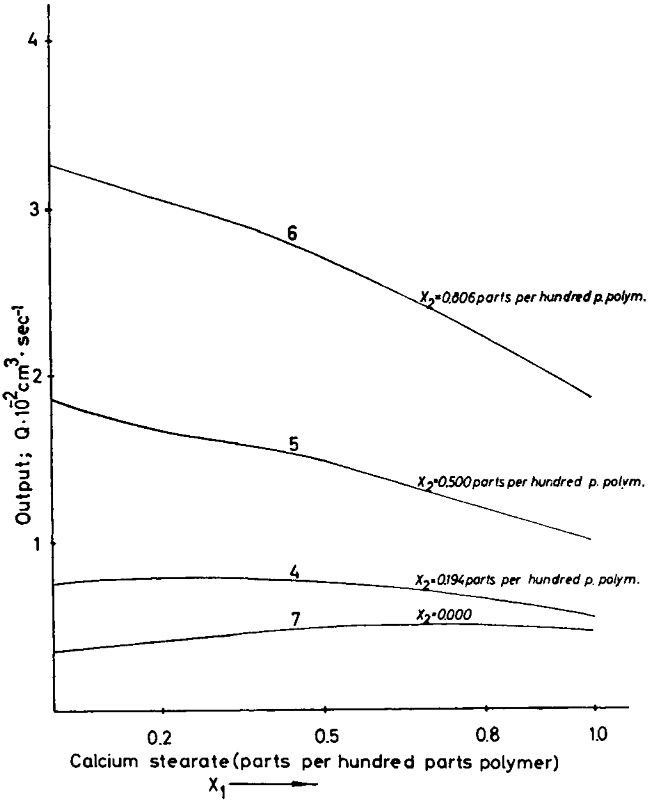

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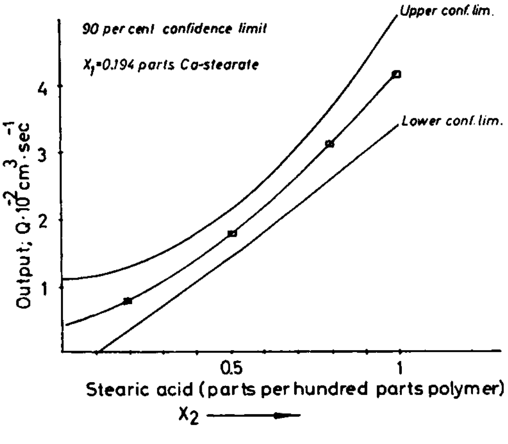

Figure 7.

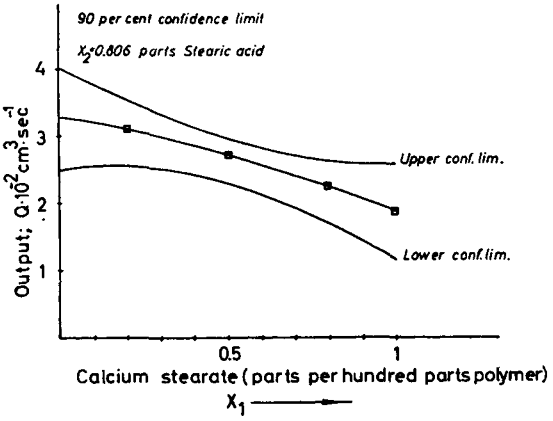

Figure 8.

Theory

The volumetric flow rate Q, shear stress τ, shear rate γ, and the apparent viscosity η for the capillary rheometer are calculated from the measured values of pressure, output, and the dimensions of the cylindric capillary.

For a Newtonian fluid the ratio τ/γ is a constant μ, named the viscosity coefficient. When a capillary of circular cross section is used, there is a linear relationship between the shear stress and the capillary radius:

$$\tau = RP/2L \tag{1}$$

where R is the capillary radius, P is the pressure differential, and L is the length of the capillary. This relationship is valid also for non-Newtonian fluids.

There is a linear relationship between the shear rate and the capillary radius for a Newtonian fluid only, leading to eq. (2):

$$\gamma = 4Q/\pi R \tag{2}$$

where Q is volumetric flow rate.

According to Rabinowitch[2] it is possible to correct for the pseudoplastic behavior of the plastic melt, thus

$$\dot{\gamma} = [(3n + 1)/n]\ (Q/\pi\ R) \tag{3}$$

where $\dot{\gamma}$ is the corrected shear rate and n is the slope of the curve generated by plotting log τ as a function of log γ. The factor n changes and has to be determined for each measured value of shear stress.

The following rheological parameters were measured and calculated: volumetric flow rate Q, corrected shear rate $\dot{\gamma}$, and the corrected apparent viscosity $\dot{\eta} = \tau/\dot{\gamma}$.

Results and Discussion

The relationship between Q and $\dot{\gamma}$ and the variables is given by the quadratic equation:

$$Z = A + BX_1 + CX_2 + DX_3 + EX_1^2 + FX_1X_2 + GX_1X_3 + HX_2^2 + IX_2X_3 + JX_3^2 \quad (4)$$

Tables III and IV show the coefficients for the equations calculated for various levels of shear stress. The values for the apparent viscosity are calculated by using the relation:

$$\dot{\eta} = \tau/\dot{\gamma} \quad (5)$$

The equations permit calculation of rheological data for any calcium stearate–stearic acid–temperature combination within the experimental limits. To facilitate the interpretation of the data, the equations in Tables III and IV were solved for some combinations of the variables; the results are shown in Figures 2, 3, and 4.

Figure 2 shows the corrected apparent viscosity contours as function of

TABLE III
Coefficients for Volumetric Flow Rate Q

	$\tau = 4.2$ kp/cm^2	$\tau = 5.6$ kp/cm^2	$\tau = 7.0$ kp/cm^2
Constant term A	-1.401	-2.854	-1.660
Coefficients			
B	1.391×10^{-1}	5.460×10^{-1}	7.295×10^{-1}
C	-3.059×10^{-1}	-8.121×10^{-1}	-1.514
D	1.481×10^{-2}	3.028×10^{-2}	1.606×10^{-2}
E	-2.803×10^{-3}	-1.202×10^{-2}	-3.775×10^{-3}
F	-1.876×10^{-2}	-5.003×10^{-2}	-5.617×10^{-2}
G	-7.298×10^{-4}	-2.828×10^{-3}	-3.949×10^{-3}
H	2.105×10^{-2}	1.970×10	3.705×10^{-2}
I	1.760×10^{-3}	4.710×10^{-2}	8.725×10^{-3}
J	-3.904×10^{-5}	-8.022×10^{-5}	-3.775×10^{-5}

TABLE IV
Coefficients for Corrected Shear Rate $\dot{\gamma}$

	$\tau = 4.2$ kp/cm^2	$\tau = 5.6$ kp/cm^2	$\tau = 7.0$ kp/cm^2
Constant term A	-1.582×10^{4}	-3.590×10^{4}	1.122×10^{4}
Coefficients			
B	3.634×10^{3}	4.582×10^{3}	2.028×10^{4}
C	-5.155×10^{3}	-9.775×10^{3}	-3.567×10^{4}
D	1.630×10^{2}	3.745×10^{2}	-2.001×10^{2}
E	-4.388×10^{1}	-1.802×10^{2}	1.228×10^{2}
F	-3.253×10^{2}	-4.376×10^{2}	4.603×10^{1}
G	-1.924×10^{1}	-2.388×10^{1}	-1.136×10^{2}
H	1.818×10^{2}	2.980×10^{2}	8.743×10^{2}
I	2.997×10^{1}	5.710×10^{1}	2.009×10^{2}
J	-4.181×10^{-1}	-9.720×10^{-1}	7.780×10^{-1}

varied calcium stearate–stearic acid ratios at 185°C and $\tau = 4.2$ kp/cm^2. The corresponding curves for the corrected shear rate $\dot{\gamma}$ and the volumetric flow rate Q are shown in Figures 3 and 4, respectively. From this information it is possible to draw conclusions concerning the effect of the lubricants on the flow properties. If the content of stearic acid is increased in formulations with different constant levels of calcium stearate, the corrected apparent viscosity $\dot{\eta}$ will decrease. This leads to a corresponding increase of the corrected shear rate $\dot{\gamma}$ (Fig. 3) and the volumetric flow rate Q (Fig. 4). By replotting Figure 4 as shown in Figure 5 this trend is more clearly demonstrated. The lubricating effect of stearic acid decreases with increasing contents of calcium stearate in the formulation.

On the other hand, increasing amounts of calcium stearate at different constant levels of stearic acid lead (Figs. 2–4) to an increased corrected apparent viscosity $\dot{\eta}$ and a decreased corrected shear rate γ and volumetric flow rate Q. This effect appears more clearly in Figure 6, which is a replot of Figure 4. This figure indicates that the effect of calcium stearate becomes more pronounced with increasing contents of stearic acid in the formulation.

Figures 7 and 8 indicate the reliability of the results. The 90% confidence limits are shown. Based on the analysis of reliability the effect of stearic acid on the flow properties seems very pronounced. However, as to the effect of calcium stearate on the flow behavior, the confidence calculations do not indicate a strong dependence. As can be deduced from the equations in Table III, the mentioned effects are not only found for selected combinations of the variables and the shear stress shown in Figures 2–8. Similar trends are found over most of the experimental range, including the lubricant combinations actually used for twin screw extrusion of rigid PVC pipes (calcium stearate 0.2–0.8 parts, stearic acid 0.2–0.8 parts per hundred parts polymer).

Within this area the influence of calcium stearate is opposite to the normal characteristic of a lubricant. Since calcium stearate is used extensively in formulations for rigid PVC extrusions, this effect seems rather contradictory. In the extrusion of rigid PVC, the apparent "lubricating" effect of calcium stearate is probably to produce in creased friction with resulting heat evolution and higher mass temperature, leading to decreased viscosity of the plastic material.

For the extrusion experiments the same basic formulations were used as for the rheometer measurements. Tables V and VI show the lubricant combinations used for these trials and the results based on extrusions with dry blends and granulate respectively.

In spite of the uncertainties of some of the results, an increasing amount of calcium stearate appears to reduce the back pressure, as shown in Table VI. The results in Tables V and VI show no clear trend regarding the effect of calcium stearate on the back pressure and the influence of both lubricants on the output.

The effect of the lubricants on the mass temperature and the power con-

TABLE V
Dry Blend

Stearic acid, pph	Calcium stearate pph	Back pressure, kp/cm^2	Mass temperature, °C	Power consumption kw	Output, kg/hr
0.00	0.25	2300–2500	201–203	1.65–1.75	9.2–9.8
0.00	0.50	2500–2250	201–200	1.65–1.55	9.0–8.2
0.00	0.75	2475–2250	199–200	1.70–1.60	9.1–8.5
0.00	1.00	2450–2750	200	1.50–1.60	8.5–9.1
0.10	0.00	2700–2450	194	1.15–1.10	10.7–10.4
0.10	0.25	2850–2800	201–202	1.60–1.25	9.8–10.8
0.10	0.50	2700–2450	199–198	1.55–1.45	9.5–10.0
0.10	0.75	2500–2750	203	1.60–1.50	9.0–9.8
0.10	1.00	2500–2800	201–202	1.65–1.50	9.2–10.0
0.30	0.00	2075	182–183	0.90	10.8–11.2
0.30	0.25	2250	187	0.90	10.5–10.8
0.30	0.50	2400	190	1.00	10.3–10.7
0.30	0.75	2450	190	1.10	10.6–11.2
0.30	1.00	2650	195	1.40	10.1–10.5
0.00	0.00	2850–3200	204–202	1.55–1.70	9.6–10.1
0.40	0.00	1800–1900	180–178	0.85	11.0–11.3
0.40	0.25	1200–1550	181	0.85–1.00	7.9–8.9
0.40	0.50	1500–1800	184	0.92–1.02	8.0–9.6
0.40	0.75	1850–2200	187–190	1.10–1.20	10.0–11.0
0.40	1.00	2100–2300	196	1.30–1.40	10.2–10.7

TABLE VI
Granulate

Stearic acid, pph	Calcium stearate, pph	Back pressure, kp/cm^2	Mass temperature, °C	Power consumption, kw	Output, kg/hr
0.00	0.00	2250–2400	203	1.4–1.5	5.1–5.3
0.00	0.25	2100–2050	201–200	1.5–1.4	4.9–4.7
0.00	0.50	2100–2000	205	1.5–1.4	5.0–4.8
0.00	0.75	2100	205	1.5	4.7–4.9
0.00	1.00	2050–2125	205	1.5	4.7–4.9
0.10	0.00	2200–2450	202–204	1.6	5.0–4.8
0.10	0.25	1700–1850	202	1.5–1.4	5.1–5.4
0.10	0.50	1800–1650	203–204	1.5–1.4	5.2–4.7
0.10	0.75	1900–2000	205	1.6–1.5	5.2–4.8
0.10	1.00	2050–2125	205	1.4–1.5	5.0–4.7
0.30	0.00	1350	190	1.1	6.5–6.7
0.30	0.25	1200	190	1.0	6.1–6.5
0.30	0.50	1550	196	1.1	6.0–6.3
0.30	0.75	1750–1500	204–203	1.3–1.2	6.1–5.5
0.30	1.00	2050–1800	206	1.3	6.0–5.5
0.60	0.00	1225–1350	183	0.7	5.2–5.4
0.60	0.25	1100	184–185	0.75	5.2–5.4
0.60	0.50	1000	187	0.85	5.7–5.9
0.60	0.75	1200	189	0.90	5.9–6.1
0.60	1.00	1500	190	1.0	6.0–6.3

sumption is however, very conclusive. This is shown in Figures 9 and 10. Addition of increasing amounts of stearic acid causes a reduction in both mass temperature and power consumption. This effect decreases with increasing amounts of calcium stearate in the formulations.

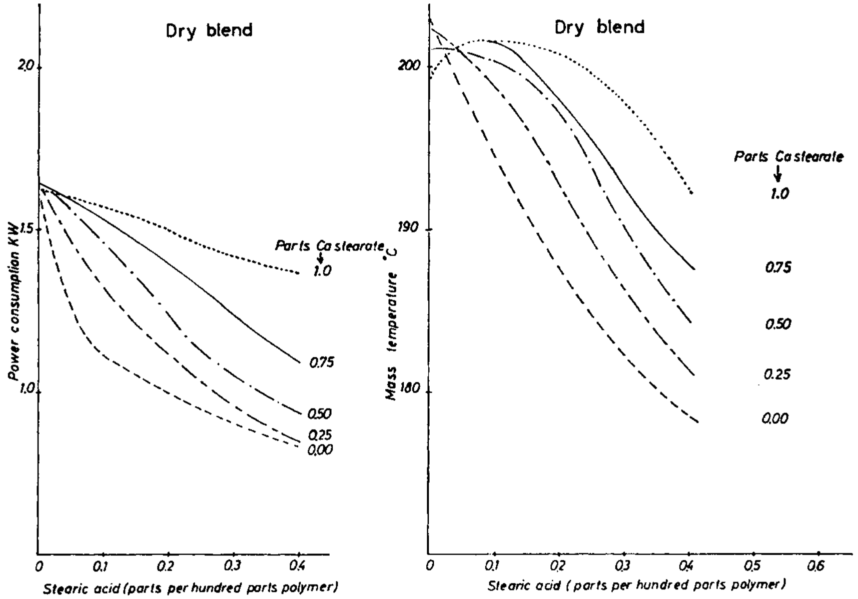

Figure 9.

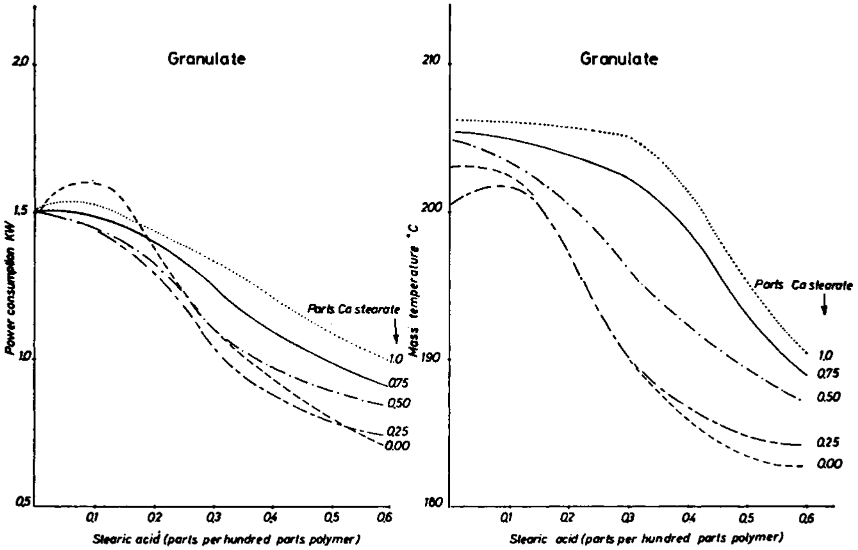

Figure 10.

On the contrary, addition of calcium stearate leads to a higher mass temperature and power consumption. This effect increases with increasing amounts of stearic acid added to the formulation.

The measured trends concerning mass temperature and power consumption are in agreement with the results obtained by the rheometer measurements. The extrusion experiments confirm that stearic acid reduces the melt viscosity and acts as an ordinary lubricant, while calcium stearate leads to increased friction and higher mass temperature.

Conclusions

Capillary rheometer measurements show that stearic acid acts as a normal lubricant, resulting in lowered melt viscosity of the rigid PVC formulation. Addition of calcium stearate has the opposite effect, leading to a higher melt viscosity. The effect of stearic acid decreases with increasing contents of calcium stearate, while the effect of calcium stearate increases with increasing amounts of stearic acid in the formulation.

The apparent "lubricating" effect of calcium stearate when extruding rigid PVC is probably due to an increased friction leading to a higher mass temperature. In agreement with this hyothesis and with the rheometer results, the extrusion experiments show that both mass temperature and power consumption decrease with addition of stearic acid and increase with addition of calcium stearate to the formulation.

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