

PVC Powder Extrusion. Melting Properties and Particle Morphology

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Synopsis

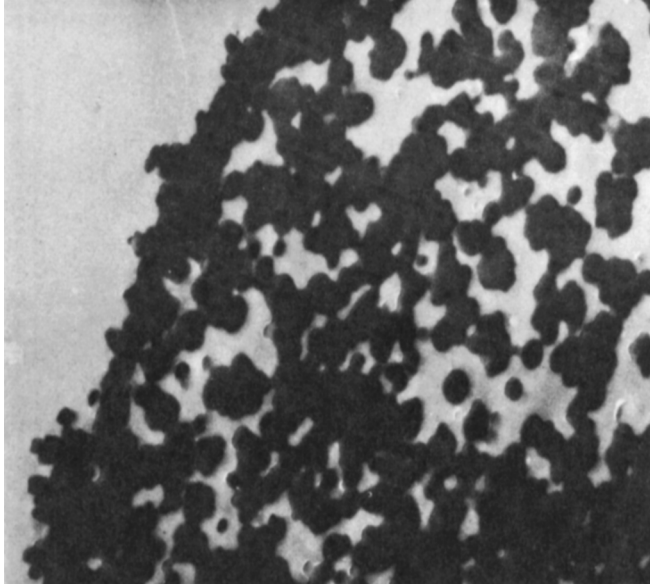
The extrusion of unplasticized PVC powder has been studied. Powder blends with low amounts of lubricants have been used in order to observe differences between structurally different PVC powders. Experiments with varying screw speeds indicate that resins consisting of agglomerated, small, globular primary particles are more sensitive to shear and deformation in the extruder channel than more compact particles. Frictional heat seems to be dissipated inside loosely agglomerated resin particles, possibly because of a larger internal surface. This additional heat, which depends on the shear rate, influences the melting behavior considerably. Scanning electron microscopy shows that PVC particles seem to melt without first breaking into smaller particles. A comparison between bulk-polymerized and suspension-polymerized PVC with nearly the same particle structure reveals a close similarity in melting properties. The results obtained in this work indicate that structural differences may explain the differences in melting behavior often observed when rigid PVC blends are extruded.

INTRODUCTION

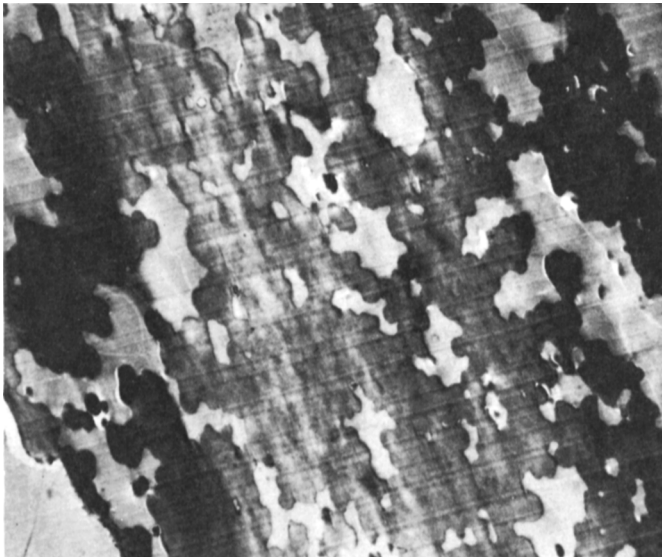
When granules of polyethylene and plasticized poly(vinyl chloride) were extruded, Maddock¹ found that particles in contact with the barrel melted and smeared a molten film over the barrel surface. The melted material collected against the pushing face of the screw flights, while the forward portion of the channel was filled with unmelted material. According to Street,² the rate of melting is related primarily to the contact surface between melted and unmelted material, the temperature of that surface, and the way in which the material is contacted against it. With a small laboratory extruder, Gregory³ found that the conductive heat supplied from the barrel represents only a small percentage of the total energy required to melt the polymer (0%–20%). The mechanical energy dissipated must therefore make up the difference if the extruder is to operate properly. The mechanical heat arises from viscous shear and through deformation of the solid polymer. According to Bernhardt,⁴ heat is evolved in internal shear within the gross body of the material when powders or small granules are conveyed in an extruder.

In spite of the growing importance of PVC dry blend extrusion, especially with unplasticized formulations, little is published. Berens et al.⁵ related melt flow properties to the particle structure of emulsion- and suspension-polymerized PVC resins. Based on Brabender measurements, Omacini and Gatta⁶ concluded that emulsion resins are easier to process than suspension PVC because of particle size, shape, and adhesive forces between their primary particles. Differences in bulk densities may explain why fusion time was found to decrease with increasing average dimension of the polymer particles. Hattori et al.⁷ have studied

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(a)



(b)

Fig. 1. Electron microscope pictures of the resins: (a) resin A (3300 \times); (b) resin B (3300 \times); (c) resin C (5200 \times).



(c)

Fig. 1. (Continued from previous page).

the structure of extruded PVC materials by an MMA embedding technique combined with electron microscopy. They concluded that the PVC resin particles were broken down to primary particles during extrusion. The primary particles were then further broken down to what they called fibrils.

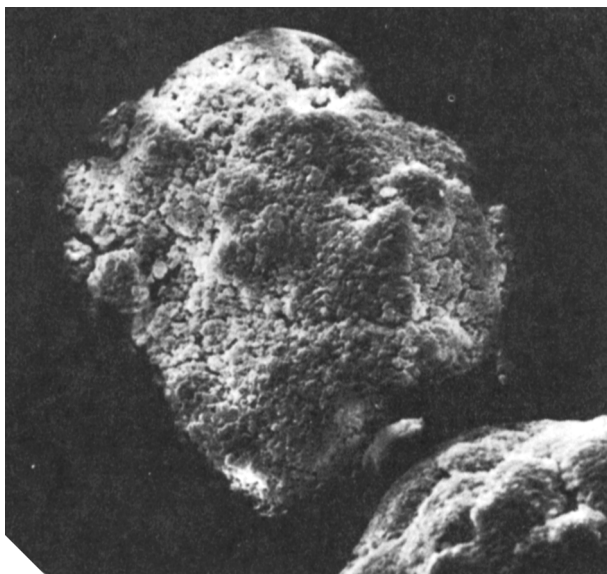
Suspension- and bulk-polymerized PVC resin particles are built up by primary particles with diameters in the $0.2\text{--}2\ \mu$ region.⁷⁻¹¹ The primary particles may be (1) agglomerated to larger particles without losing their globular character; (2) tightly agglomerated, thus losing their individuality because the interface has more or less disappeared. These two main differences between PVC particle structure are observed by use of electron microscopy (EM) and scanning electron microscopy (SEM).

EXPERIMENTAL

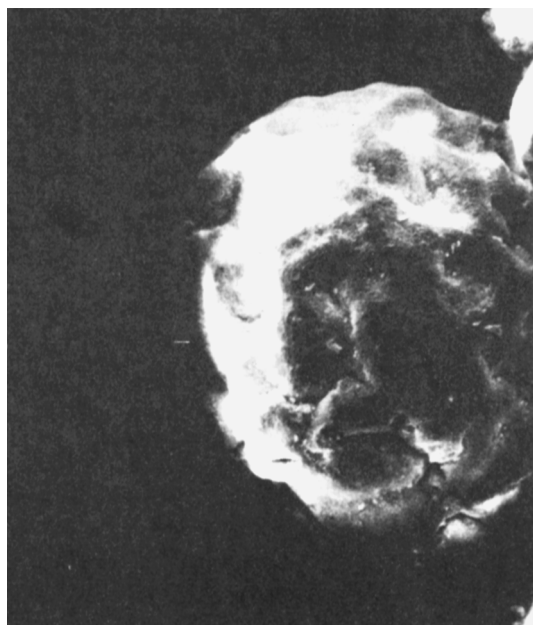
Description of the PVC Resins

EM and SEM pictures of the particles were taken. For EM pictures resin particles were embedded in unsaturated polyester (Vestopal) which was then cured. Specimen were cut $700\ \text{\AA}$ thick with a microtome. The SEM pictures were taken with a JSM-U3 (JEOL) after a coating of gold (about $200\ \text{\AA}$ thick) had been deposited on the particles.

Three resins were used. Resin A was a bulk-polymerized resin. The particle structure can be classified as belonging to group 1 mentioned before. Medium particle diameter was $115\ \mu$. Figure 1(a) shows an EM, Figure 2(a) an SEM picture of resin A particles. Resin B was suspension polymerized having a

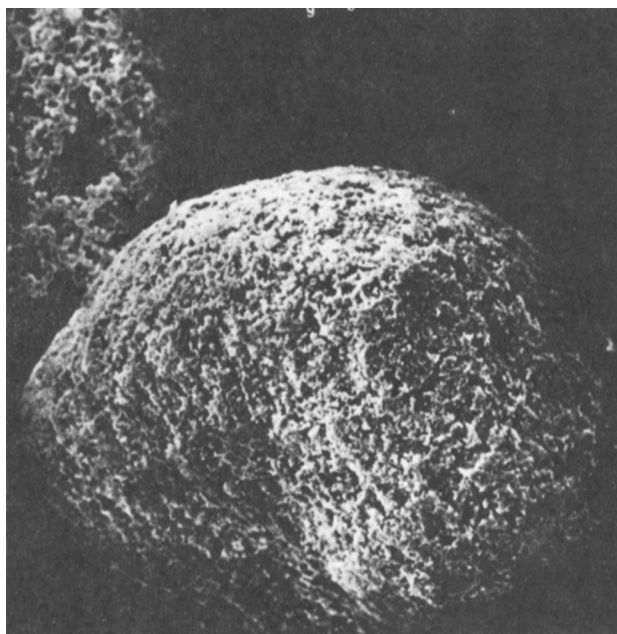


(a)



(b)

Fig. 2. Scanning electron microscope pictures of the resins (600 \times): (a) resin A; (b) resin B; (c) resin C.



(c)

Fig. 2. (Continued from previous page).

particle structure belonging to group 2. Medium particle diameter was 100 μ . An EM picture is shown in Figure 1(b) and an SEM picture, in figure 2(b). Resin C was suspension polymerized. Medium particle diameter was 100 μ . Figure 1(c) shows an EM picture of the resin and Figure 2(c), an SEM picture which clearly reveals the similarity between this resin and resin A.

The difference in porosity was measured using standard nitrogen adsorption. Resin A has a specific area of 0.95 m²/g, resin B, of 0.34 m²/g, and resin C, of 1.46 m²/g. Molecular weights and molecular weight distributions, determined by GPC (Waters 200), were nearly the same for all the resins (Table I).

Dry blends of the resins were prepared in a Papeinmeier mixer heated to 120°C. The following formulation was used: PVC, 100.0 parts; tribasic lead sulfate, 1.5 parts; dibasic lead stearate, 1.5 parts; calcium stearate, 0.5 parts; stearic acid, 0.2 parts.

TABLE I
GPC measurements of PVC resins

Resin	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
A	92 000	44 000	2.1
B	91 300	40 000	2.3
C	91 000	42 000	2.2

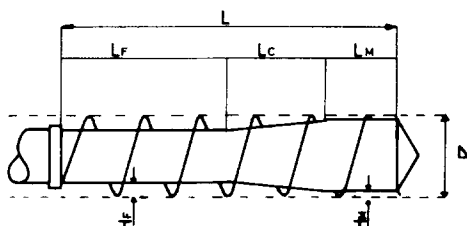
Procedure

A 30-mm electrically heated, single-screw laboratory extruder with L/D ratio 15:1 was used. The extruder was equipped with a removable barrel. The back pressure could be controlled by a movable slit. The temperature in the melt was measured using an iron/Constantan thermocouple mounted at the front end of the extruder. The screw used had the characteristics shown in Figure 3.

Extrusion temperatures were set at 145°, 170°, 185°, and 185°C. The back pressure was kept constant (400 kp/cm²) during the experiments. In order to get different shear rates, the resins were extruded at screw speeds ranging from 20 to 80 rpm. At these conditions the material was never completely melted in the extruder. This was deliberately chosen in order to get a better insight in melting mechanisms that may be important in the extrusion of rigid PVC. The melting behavior of the resins inside the extruder at different experimental conditions was studied by cooling experiments.¹

After the barrel was removed, the polymer helix around the screw was marked at different positions perpendicular to the flights. The axial distance from the beginning of the screw flights, near the feed hopper, to the midpoint of the marks was measured (L_M). The helix was then unwrapped from the screw and sectioned along the marks. One could visually observe two distinct phases; one consisting of a homogeneous melt; the other made up of partly melted particles, partly unmelted material, and in the feeding section of the extruder mostly compressed powder. A sharp boundary was usually found between these two phases. The area of melted material (A_M) divided by the channel cross-sectional area (A) was therefore easily determined. By plotting this ratio against the length ratio, i.e., the length measured as mentioned above divided by the length of the screw (L), was obtained melt profiles of the PVC powders at different screw speeds. A melt profile measured in this way shows how homogeneously melted material is being built up as a function of the distance from the beginning of the screw flights.

The reproducibility of the melt profiles was found to be excellent.



D	L_f/L	L_c/L	L_m/L	H_f	H_m
30 mm	0-0,5	0,5-0,8	0,8-1,0	5,2 mm	2,0 mm

Fig. 3. Description of the extruder screw.

RESULTS AND DISCUSSION

Extrusion Experiments

The melt profiles obtained when resins A and B were extruded at different screw speeds are shown in Figures 4 and 5. Profiles obtained when resin C was extruded had the same general appearance as resin A and are therefore left out.

The melting process starts in the feed section of the screw. The initial rate of building up homogeneously melted material is nearly the same for all the resins at any screw speed. The barrel temperature will be nearly the same in the region where melting starts at the different screw speeds applied. The heat transfer from the barrel, therefore, is important for the initial melting, while the resin particle structure has little if any influence.

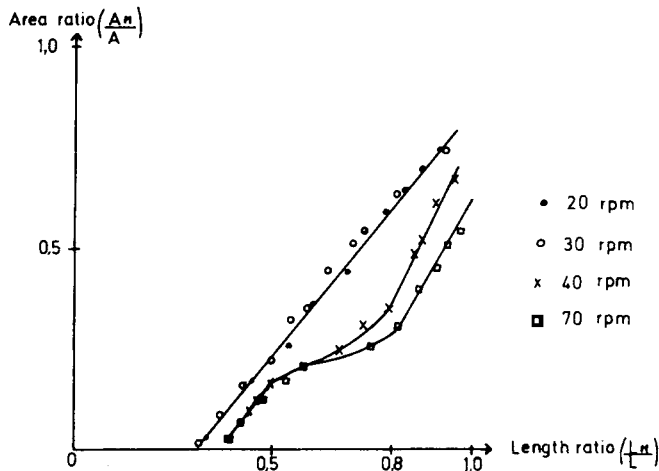


Fig. 4. Melt profiles obtained for resin A at different screw speeds.

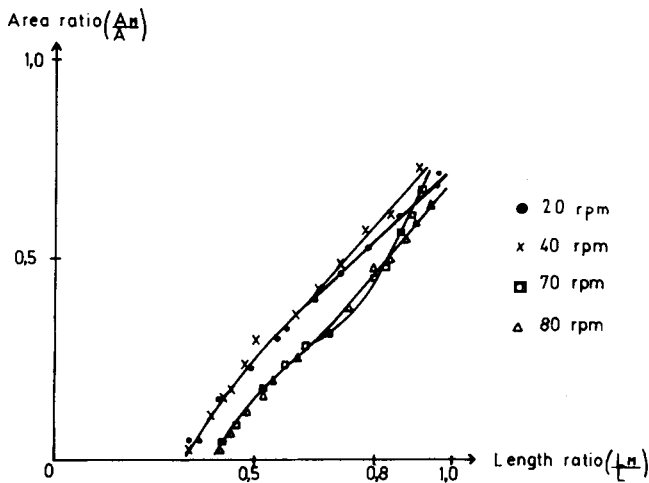


Fig. 5. Melt profiles obtained for resin B at different screw speeds.

In the compression section of the screw (length ratio 0.5–0.8) there is a distinct difference between the resins. From approximately 40 rpm, resin A has a pronounced decrease in the rate of building up homogeneously melted material.

In the metering section of the screw (length ratio 0.8–1.0), the melt profiles are nearly linear. By graphically determining the slope of the melt profiles in this section, we obtained the results which are shown in Fig 6. This is an expression of the rate by which homogeneously melted material is built up as a separate phase in the metering section. The similarity between resins A and C is evident in this figure. These resins reach a maximum value for this slope at approximately 40 rpm. Resin B, however, has a maximum value in the 60–70 rpm region.

Since the flow rates were nearly the same for these resins at the same screw speed (± 0.3 kg/hr), the heat delivered from the barrel is approximately equal. The amount of shear ought to be nearly the same as well when the same screw speed is used.¹² The reason for the increased rate by which homogeneously melted material is observed in the metering section for resins A and C at 40 rpm can be explained, however, if more heat is supposed to be generated when resins of this morphology are extruded compared to a resin with a more compact particle structure at the same conditions (resin B). This means that in addition to heat supplied from the hot barrel and from viscous shear of the molten polymer, there must be a heat supplement which depends upon resin particle structure and shear rate.

This is supported by an interesting observation made when extrusions were carried out at 80 rpm. In Figure 7, photographs of sectioned pieces of the melt helix obtained at this screw speed are shown. According to Menges,¹³ the flow behavior found for resin B is normal for a highly viscous material. The melt is observed at the passive side of the screw flight (to the left in the pictures). This was found for all resins at lower speeds. At 80 rpm the flow of resins A and C is normal for a highly viscous material in the feed section of the screw. In the compression section, the melted material changes to a position at the pushing face of the screw flights, and in the metering section a flow behavior normally seen when materials of low viscosity are processed (e.g., plasticized PVC and PE).

A considerable temperature increase in the compression section causing a

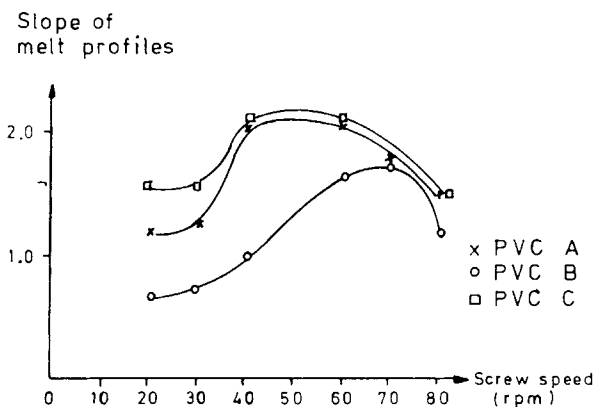


Fig. 6. Slope of melt profiles in the metering section of the screw at different screw speeds.

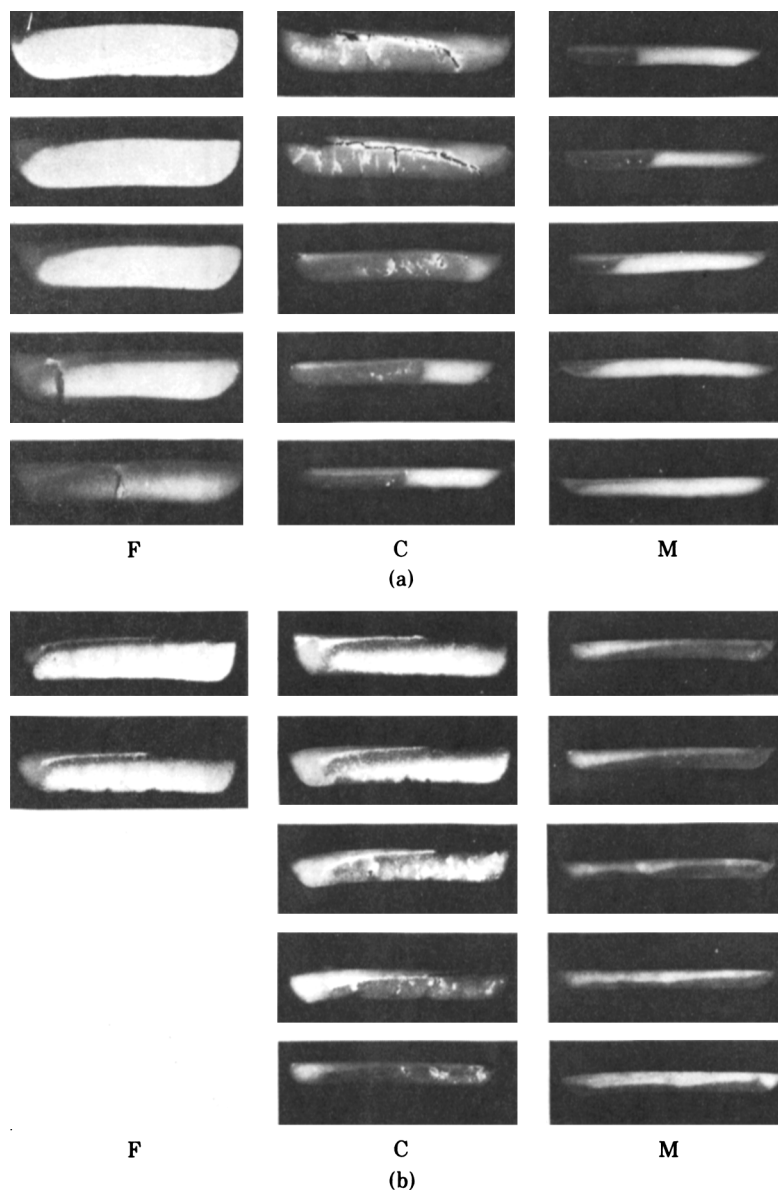


Fig. 7. Sectioned pieces of the melt helices from the feed section (F), compression section (C), and metering section (M) of the screw. Screw speed, 80 rpm: (a) resin A; (b) resin B.

decrease in viscosity during extrusion of resins A and C compared to resin B would explain this. Extrudate temperatures measured at different screw speeds support this (Fig. 8), as resins A and C do have higher extrudate temperatures than resin B.

Extrudate temperatures obtained when cylindrical pellets of the resins were extruded at the same conditions show that the temperature differences observed when powders were extruded are almost eliminated (Fig. 9). Differences in particle structure are more or less eliminated when the resins are pelletized. Flow rates were 1–2 kg/hr less when pellets were extruded, therefore the temperature

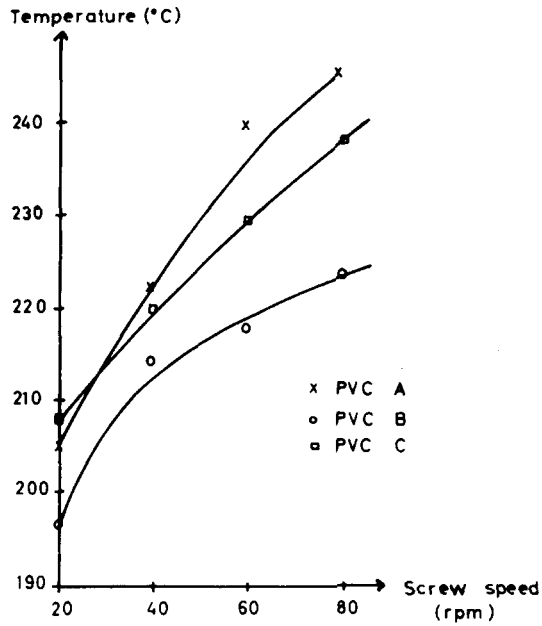


Fig. 8. Extrudate temperatures obtained when PVC powders were extruded at different screw speeds.

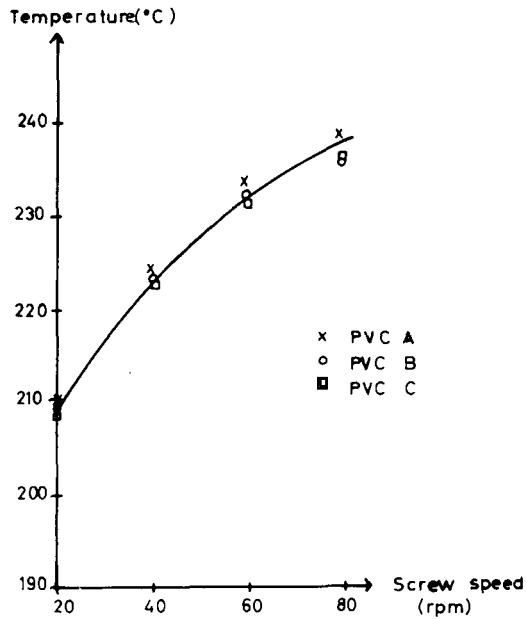


Fig. 9. Extrudate temperatures obtained when PVC pellets were extruded at different screw speeds.

curves in Figures 8 and 9 are not directly comparable. This does not, however, affect the conclusion.

Scanning Electron-Microscopic Studies

In order to study details during the melting of the PVC particles, melt helixes obtained at 40 rpm were studied by scanning electron microscopy. In contrast to the earlier experiments the melt helix was broken by hand and the fractured surface studied in the different screw sections.

In the feed section of the screw, unmelted particles of a more or less edged form (due to compression) were observed. Pictures of resin A from the compression section, $L/D = 0.65$, are shown in Figures 10 and 11. In Figure 10 it is still possible to identify the individual PVC particles. The particles are deformed but not disintegrated into the primary particles as described by other authors.⁷ The picture in Figure 11 is taken near the melt pool. In spite of still being able to identify individual PVC particles, the inner structure of some particles have melted and we can observe cracks propagating in melted material.

Since these pictures were representative for resin C as well, particles of this morphology seem to develop heat internally when the resin is sheared or compressed, resulting in an *intraparticular* fusion. A possible reason for this is the large frictional surface inside resin particles composed of small agglomerated, primary particles. Heat developed in this way will be uniformly distributed in the melting particles. This tendency to *intraparticular* fusion will not be noticeable when determining the melt profiles in the compression section because the particles still look like they have not melted; i.e., little *interparticular* fusion (Fig. 10). This is the main reason why the rate of buildup of a homogeneous melt is judged to decrease in the compression section (Fig. 4). In the metering section, the higher temperature caused by compression, and the improved mixing of melted and partly melted polymer, result in a sharp increase in the rate of building up of a homogeneous melt.

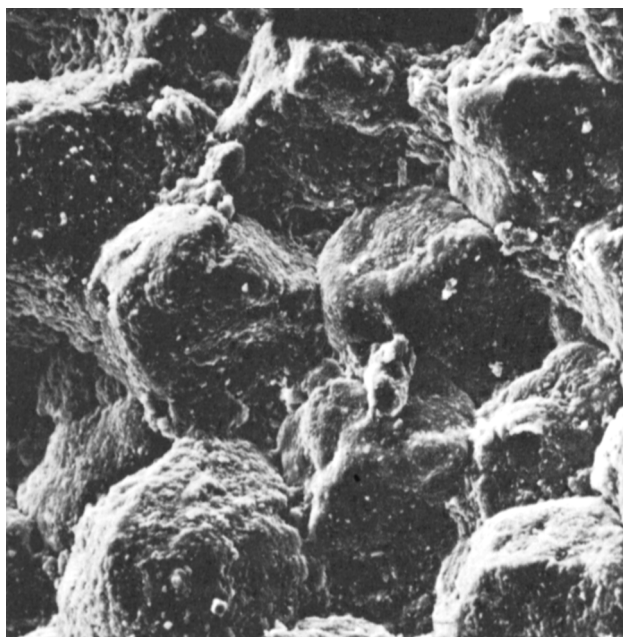


Fig. 10. Melting resin A particles. Electron microscope picture from the compression section of the screw (300 \times).

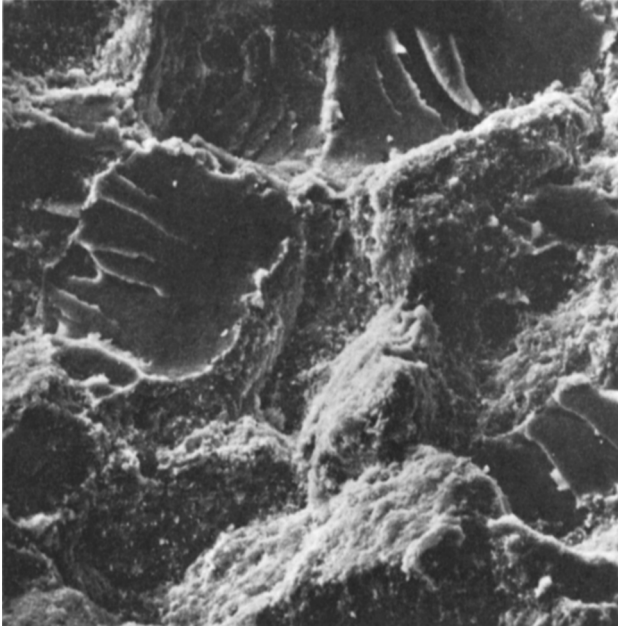


Fig. 11. Melting resin A particles. Electron microscope picture obtained from the compression section near the melt pool (300 \times).

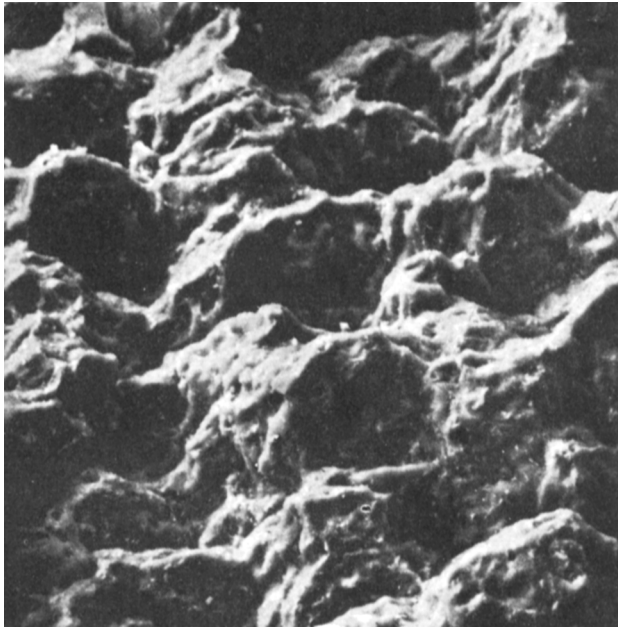


Fig. 12. Melting resin B particles. Electron microscope picture obtained from the compression section (300 \times).

A representative picture of resin B in the compression section is shown in Figure 12. In contrast to what was observed for resins A and C, these particles lie in a melt pool. Because of the more compact structure of resin B particles,

little heat is believed to be generated internally. Melting then starts in the outer regions of the resin particles. Small resin particles and irregularities in the particle surface thus give a melt which "lubricates" the melting polymer and reduces the amount of heat otherwise produced by compression and shear. The melting process for resin B compared to resin A and C depends more on heat transfer from the barrel and from viscous shear of the homogeneously molten polymer.

CONCLUSIONS

Extrusion experiments have shown that PVC resin particle structure has no influence on melting behavior in the feed section of a screw. In the compression section, however, resin particle structure has a strong influence. More heat is generated in the compression section of the screw when resin particles consisting of agglomerated globular primary particles are processed than when a resin of a more compact particle structure is extruded.

Scanning electron microscopy indicates that when loosely agglomerated resin particles are extruded, heat is generated inside the particles when the resins are compressed and sheared. This frictional heat is an important supplement to conductive heat from the barrel and heat generated from viscous shear of the melt. It probably arises because of the large frictional inner surface of loosely agglomerated particles compared to particles where the primary globules are more tightly agglomerated. The amount of frictional heat developed in this way will also depend on shear rate and lubricant content. When a shear rate is reached where this additional heat becomes significant, this is found to have a pronounced influence on the melting process and in fact on the flow behavior of the homogeneous melt in the barrel. The reason for this is probably that the frictional heat will be uniformly distributed in the melting polymer and therefore influence the mass temperature more than the conductive heat and the heat generated from viscous shear of the polymer melt. Such a melting mechanism may be one reason for the big differences often observed when different PVC resins are extruded.

The melting behavior is similar when PVC resins with nearly the same morphology, particle size, particle size distribution, and molecular weight are extruded even if one is suspension polymerized and the other bulk polymerized.

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