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POLYVINYL CHLORIDE - PROCESSING AND STRUCTURE

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Abstract - Widely different procedures for the processing of PVC have proved themselves and have succeeded in practice on the basis of the special physical and chemical properties of PVC. In this connection a distinction must be made between the processing of plasticized PVC and the relatively difficult processing of rigid PVC. A survey of the most important methods of preparation and processing is given here.

The special, rather abnormal properties of PVC in comparison with other thermoplastics are partly a result of its characteristic structure. The consequences for preparation and processing must therefore be considered anew. Of course, the globular structure of PVC has an effect on the behaviour of the solid-state material and the melt, too, so that great importance must be attributed to the processes at the particle interface.

1. INTRODUCTION

Though polyvinyl chloride has been in existence for a long time far less is known about it than about the comparatively new polyolefins. It is incomparably more difficult to process because of its low decomposition temperature, a fact which impedes laboratory tests, too. Many research workers say that chlorine begins splitting off just above 100°C (1,2,3). It shows the lowest activation energy for decomposition of all plastics, except for PVA (4).

It can be attributed to its low raw-material price - it is a typical recycling product of the chemical joint utilities - as well as to its excellent compatibility with bad low-molecular solvents, the so-called plasticizers, that PVC has nevertheless developed to become the greatest mass plastic at certain times. With these plasticizers it builds subsidiary valence gels which have an elastomeric character in the vicinity of room temperature. These so-called plasticized PVCs can easily be processed.

From table 1 where the most important thermoplastics have been listed according to their processing possibilities it can be seen that plasticized PVC has the largest processing range (5). Moreover, it can be filled with mineral powders up to 50 vol.-%. In this form it has already been used a great deal. In doing so, we have learned more and more to process it also as rigid PVC.

However, there are special processing procedures for plasticized PVC which cannot be transferred to other polymers, e.g. the processing of pastes (see table 2). Today, the processing of plasticized PVC still accounts for 40 % of a processed total quantity of 1 million tons PVC in the FRG in 1974 (production capacity came to 1,3 million tons per year in the same period). The ranges of application are illustrated in figure 1. In recent years, very high increase rates could be registered in the case of rigid PVC for calendering foils as well as extruded pipes and profiles.

The ranges of application are very much connected with its elastic behaviour. Thus figure 2 gives an excellent survey of the ranges of application and of the influence of added plasticizers - the log. curve of the modulus of shear over the temperature.

The kind of raw-material production has a considerable influence on the workability. As can be seen from table 2 certain kinds of raw material production and certain molecular weights (K-values) are associated with the different processing procedures (6). This is particulary connected with the grain structure, i.e. with

Processing / raw material	Injection-moulding	Ex-trusion	Blow-moulding	Calen-dering	Film-blowing	Foam production	Com-pression moulding	Processing of pastes
Rigid PVC	+	++	+	++	+	o	+	o
Plasticized PVC	+	++	o	++	+	+	+	++
Polyolefins	++	++	++	o	++	+	+	o
Polystyrene incl. SAN+ABS	++	+	o	o	o	+	o	o

(++ = mainly, + = to a small extent, o = not at all or in exceptional cases only)

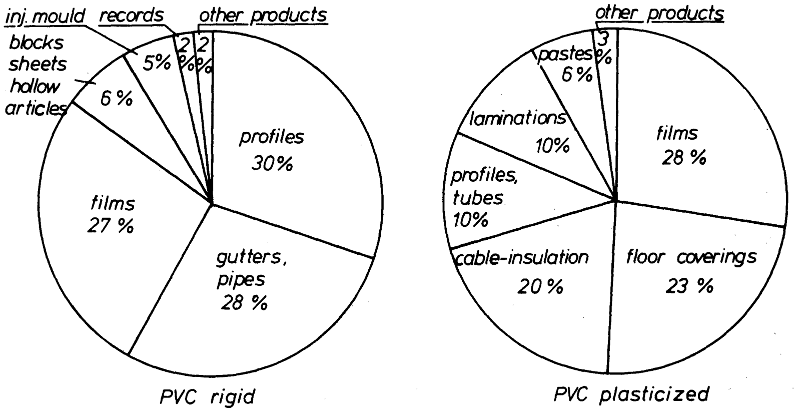
Table 1: Processing methods for plastics and the materials thus processed (according to Krüger (5)).

PVC-types / processing	rigid- PVC			plasticized – PVC		
	E	S	B	E	S	B
	K - values			K -values		
calendering	(60-65)	57-65	57-65	70-80	65-70	70
thermal refined films	75-80	-	-	-	-	-
floor covering	-	-	-	60-80	60-70	
extrusion of rigid PVC						
pressure pipes	70	67-68	67-68			
profiles	65-70	65-67	57-68			
sheets and flat films	60-65	60	60			
blown films	60	57-60	60			
extrusion of pla-sticized - PVC						
general				65-70	65-70	65-70
cable materials				-	65-80	
mainly				-	70	70
blow moulding	-	57-60	58-68		65-80	60-65
injection moulding	-	55-60	56-60	-	65-70	55-60
processing of pastes	-	-	-	70-80	(70-80)	

Table 2: Ranges of application of PVC (6).

- the porosity
- the bulk weight

as well as the contents and the distribution
- of polymerization admixtures and others.



PVC rigid PVC plasticized

Figure 1: Applications of rigid and plasticized PVC in the FRG (33)

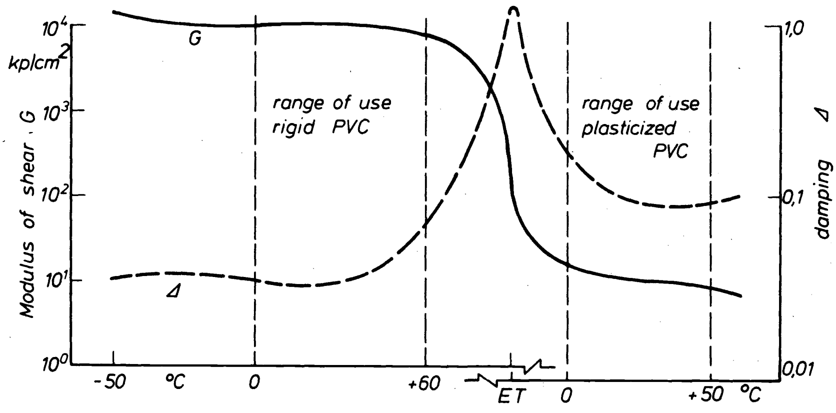


Figure 2: Ranges of application of PVC

Suspension PVC is clearly dominant in the case of extrusion but also with calendering. The compact grain structure (table 3) and the lack of polymerization auxiliaries are responsible for this. Besides E-PVC often B-PVC is used instead of S-PVC but without being able to attain the quantities of S- and E-PVC.

The emulsion PVC owes its present importance to its grain structure, too, for the grain structure absorbs the plasticizer very well because of its fissuring. Twenty years ago, the emulsifier residues served as a natural "stabilizer", particulary in the case of extrusion as rigid PVC. Today the emulsifier content is rather a disadvantage because of its hygroscopy. New procedures have very low emulsifier contents (7).

	Property	Consequences for Processing
Suspension-PVC	relatively closed grains ϕ:100 - 150 μm	free flowing properties good feed-behaviour into screws low air-content good agglomeration ability high transparency low hygroscopy good chemical resistance
Emulsion-PVC	small, rugged grains agglomeration of 0,1 - 2 μm ϕ globules to grains of < 200μm high content of polymerisation-auxiliaries	good absorption of plasticizer good gelling ability natural stabilizer

Table 3: Grain structure of PVC and effects on processing.

2. THE MOST IMPORTANT METHODS OF PROCESSING (Tables 4 and 5)

2.1 Preparation

To a great extent, PVC is prepared by the processing firms themselves, which is in complete contrast to the usual processing of thermoplastics. It is not only for historical and financial reasons that this has remained unchanged up to now in spite of all prognoses. But in this way the processing firm can derive the greatest profit from the point of view of specific workability and low costs. This is especially important in the case of this material which is very difficult to process. If you consider that a share of 2 % of stabilizer in a PVC-mixture can cost just as much as the PVC share, this becomes even more understandable. Therefore every processing firm has its own recipes which are kept strictly confidential in most cases. Nevertheless the recipes can also be classified to some extent according to the application and processing method.

Mixtures of rigid PVC contain:

100 parts of PVC
1-3 parts of powdery or fluid stabilizers
0.5-3 parts of powdery or fluid lubricants
0.1-3 parts of colouring substances
0-30 parts of impact modifiers (in most cases methacrylate or ABS basis)

Mixtures of plasticized PVC contain:

50-75 parts of (E-)PVC
45-20 parts of plasticizers (in most cases esters)
1 part of stabilizer
0.75 parts of colorants

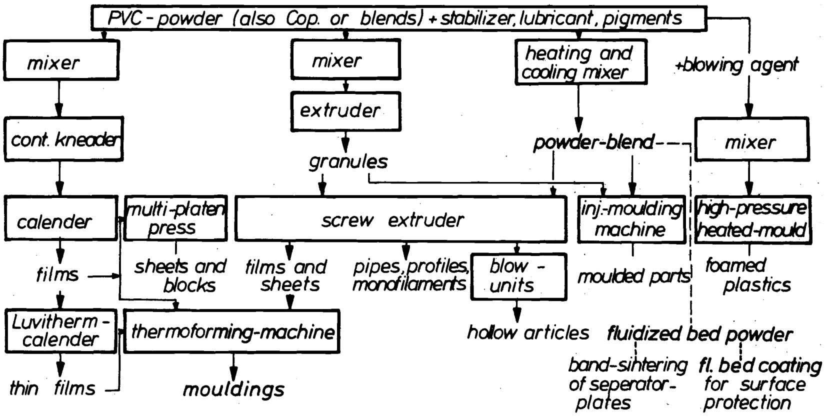


Table 4: Processing of rigid PVC (6)

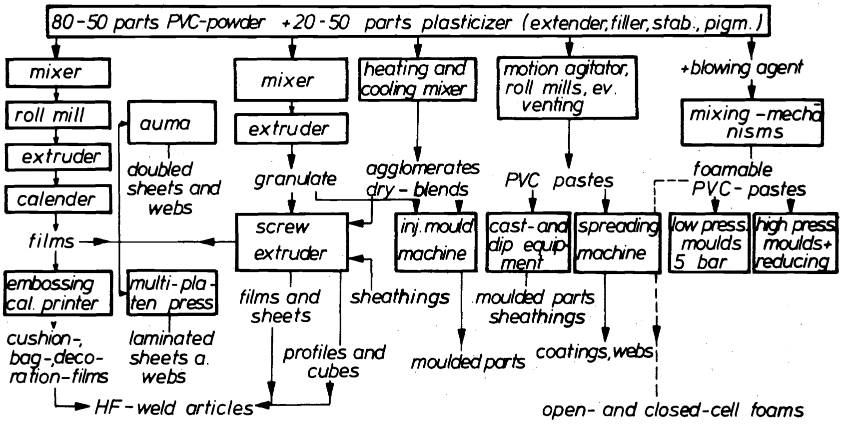


Table 5: Processing of plasticized PVC (6).

Today, the direct processing of the powder is particularly dominant because one operation can be economized on in this way, namely plasticizing with subsequent granulation. This implies not only a cost reduction, but also less thermal stress. According to Moritz (8) 95 % of all pipes, 85 % of all hollow bodies and 75 % of all Venetian blinds in PVC are processed from powder. The turbulence mixer (fig. 3) has succeeded for powder preparation followed by a cooling mixer (9,10). In the turbulence mixer the powder is not only whirled up because of the high rotation velocity of the mixing unit (40-50 m/sec), but it is also heated. A good distribution of the dry additives, which are added first, and of the liquid admixtures added right at the end, is obtained when the powder has reached about 90°C. This heating gives a free flowing dry powder or dry blend.

This procedure is also suited for the production of fluid dry blend or agglomerates with a plasticizer share of up to 40 %, if the addition of the plasticizer is effected at a temperature above the melt temperature. The warm powder absorbs the plasticizer during this process. In such plants even paste recipes can be prepared although this is rather less usual.

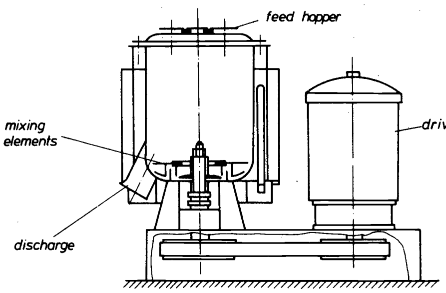


Figure 3: turbulence mixer

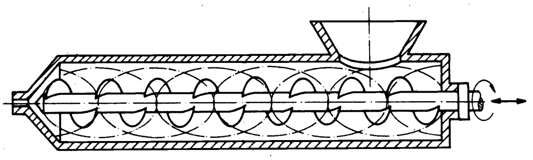


Figure 4: screw kneader

All recipes containing mineral filling materials (rock, dust, chalks) are prepared on kneading mixers which are screw kneaders today in most cases and which immediately granulate with the mounted granulator (fig. 4). In order to admix particularly large amounts of filling material the force kneader is used (internal mixer, fig. 5). (12)

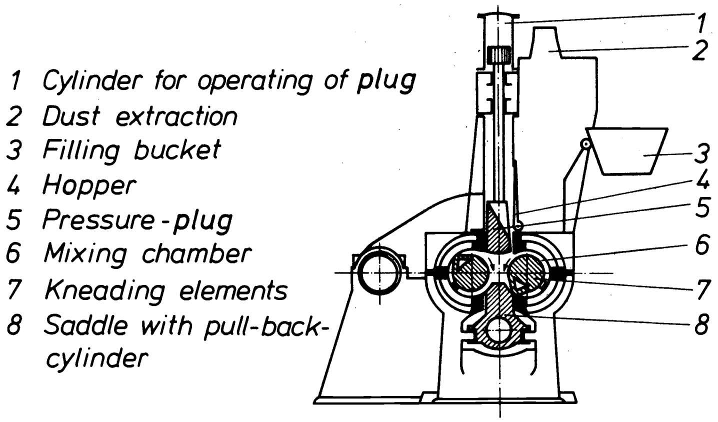


Figure 5: internal mixer

Rolling mills are still of great importance and are particularly indispensable as buffers in calender plants. Moreover, they already ventilate the mixture very well. The strips removed from them and passed to the calender have a relatively small surface only.

Pastes are sheared to a high degree in friction rollers or in dispersing plants in order to grind agglomerates of filling material. Then the paste must rest some time - ripening - so that the viscosity can increase up to the processing level by diffusing a part of the plasticizer into the PVC grains.

For pastes which are to be poured and for expandable plasticized pastes there should be deaeration in a vacuum to remove air pockets. Otherwise this air would cause undesired pores.

2.2 Extrusion

In extrusion there are distinct differences between plasticized and rigid PVC, in particular regarding the choice of extruder. While the single screw machine dominates in the case of plasticized PVC the twin screw is used in the case of rigid PVC (This is almost the only field where it is used).

2.2.1 Extrusion of plasticized PVC

Processing is unproblematic even in the case of higher filled recipes - up to 50 vol.% mineral powder can be applied - as the viscosity of the melt is already low enough at about 175°C and the heat of shear remains insignificant. Consequently the temperature of the melt itself remains below 180 - 190°C. If you have no "dead spots" in the melt stream then decomposition is not to be feared. However, it has been shown that a very good homogenization can only be attained if the melt is very well sheared. So in the cable industry which expects a high quality, of course, all screws are equipped with special shearing parts nowadays.

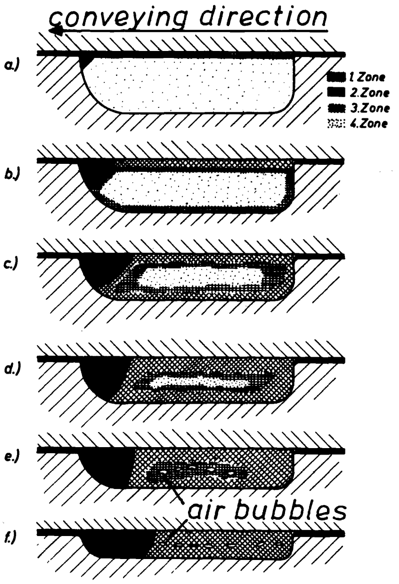


Figure 6: Course of plastification during processing of non-wall-adhesive polymers (14)

In the investigations which led to the thesis of Klenk (13) we ourselves found the reason in the recipe, especially in the outer lubricant and in the kind of stabilizer. An outer lubricant is necessary to avoid sticking but results in a "sintering-together" of the greater part of the screw-channel-volume - as fig.6 demonstrates in a model - as there does not arise any rotation stream in the pipe as occurs in the case of low viscosity and adhesive melts. While the screws can be made of nitride steels, the dies which come into contact with hot melt, must be tected by hard chromium plating.

2.2.2 Extrusion of rigid PVC

In Germany it is particularly difficult to extrude the pipe mixtures as they are permitted to contain few processing auxiliaries (DIN 8061 - DIN-German Industrial Standard -). On the other hand, in the USA more lubricants and above all up to 10 parts PMMA as impact modifier are permitted (ASTM D 1784-607). In order to take these hard conditions into account powder preparation and processing had been executed with especially short periods of dwell at a higher temperature.
Figure 7 shoes a dwell diagram derived from Brabender torque curves for a pipe mixture of rigid PVC (13).

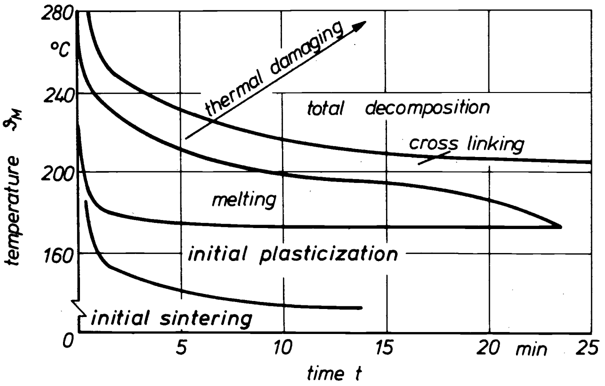


Figure 7: Dwell diagram for a pipe mixture of rigid PVC, derived from Brabender-torque curves (13)

The short and, regarding temperature, very limited zone of optimum melt can be recognized. But such a zone is necessary if a good homogenization and training of the stabilizer is to be attained. In the case of rigid PVC this is also the reason why shearing zones should be present on the extruder screw. If the stabilizer is not incorporated in the plastic zone and if the powder grains are not **destroyed** then difficulties occur in service primarily in connexion with the fastness to light.

Single screws have not so far been successful as the dominant twin screw machines - contrarotating - absorb the powder well and have forced transportation. The periods of dwell are correspondingly short (fig. 8), particulary at a high temperature as the shearing heat mainly arises immediately at the end of the screw where a backwash into the screw area arises owing to high die resistances. Here in most cases the melt is sheared sufficiently in the space between the screws (fig. 9).

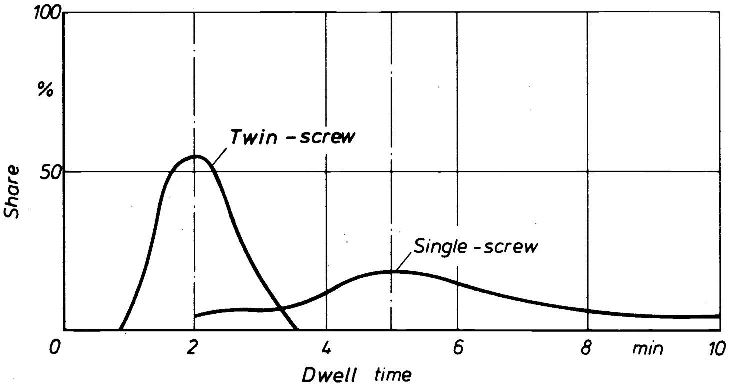


Figure 8: Periods of dwell of hard PVC on single and twin screw extruders

Almost all twin screws have had vented barrels for years. This can be done with less complications than in the case of the single screw, and thus the quality is improved owing to the absence of air pockets. However the twin screw has the disadvantage of heavy wear on cylinder and screw-depending on construction - because of the pressures in the gap. This is the reason why an enlargement of 160 mm by means of the screw diameter with output rates of 400 kg/h could not succeed though it was desirable for an hourly output of 800 kg/h in the case of large pipes. Therefore a new design works with a central screw of 250 mm and two parallel screws with a diameter of 125 mm (15).

On the other hand only single screws are usual in the case of hollow-article-blow moulding-plants owing to different recipes(proportions of impact modifier parts and tin stabilizers) which give a rather wall-like character to the melt. The same applies to the melt of expandable rigid PVC mixtures which are formed to profiles (16).

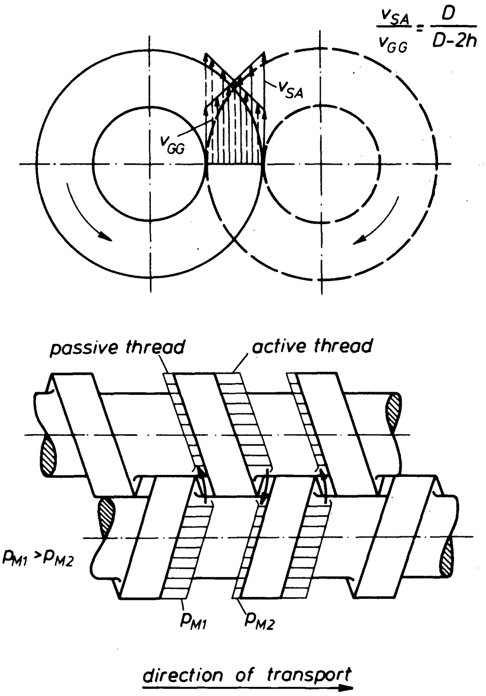


Figure 9: Velocities and pressure flows in twin screw systems (13)

2.3 Calendering

Most PVC film is manufactured by calendering and hardly any by extrusion. Here the so-called HT (high temperature) procedure is dominant (fig. 10) with high roller temperatures of up to 220°C, though the Luvitherm procedure for adhesive tape film is still used. In the case of the latter, E-PVC formulations are "sintered together" on the calender at low temperatures of a maximum of 175°C and then they are converted into the low viscosity melt state (17) for a short time in a subsequent process while passing over melting rolls at 240°C and are stretched at the same time.

The process in the calender nip of a HT plant was investigated thoroughly by us some years ago (18). The upper half of a strip running into a narrow nip (fig. 11) is peeled off in layers by the melt which has been pushed back. Thus a new surface is formed in every nip. Thus a good calender needs at least two nips. There is a trend towards 5 rollers nowadays. In many cases the foil is stretched afterwards by a subsequently added stretching section. This leads to an improvement in the mechanical qualities (tensile strength) as well as to the production of thinner foils up to about 30 µm.

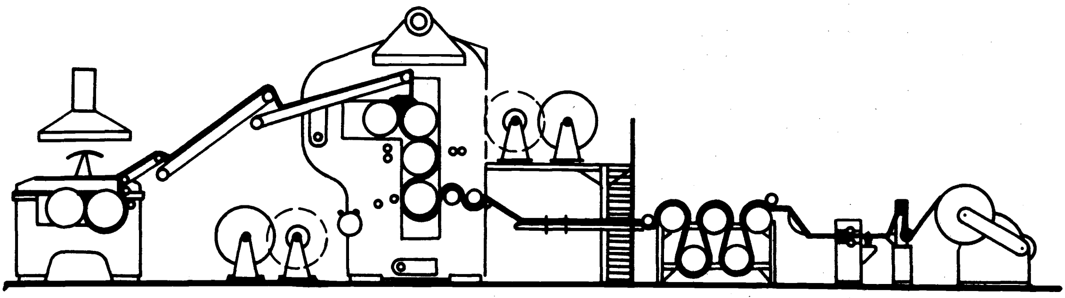


Figure 10: Calender-unit

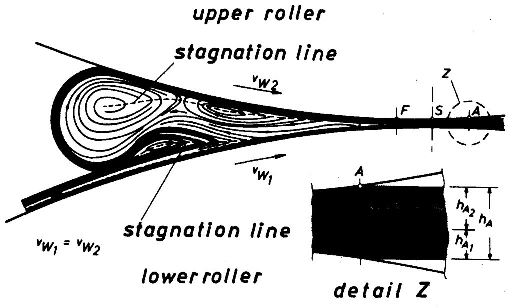


Figure 11: Flow conditions in the nip

The produktion of plasticized film corresponds to the HT-procedure, but the temperature is lower.

2.4 Injection moulding

The injection moulders have scarcely been able to get accustomed to PVC in spite of many improvements in material (19,20)and processes. To a great extent, rigid PVC is formed by injection moulding only for pipe accessories such as fittings and mountings. Plasticized PVC is used more for shoe soles which are injection moulded on round table automatic equipment today. Indeed, PVC always causes a certain corrosion because of the splitting off of HCl at the moulds which never can be avoided although the surfaces of the moulds are chromium-plated.

PVC can be injection moulded only on screw-type machines. A special screw is required, with threads extending right up to the tip.

Moreover, only open nozzles can be applied which do not possess "dead spots" in which the melt can become trapped.

2.5 The processing of pastes

This ingenious procedure is suited for PVC only. Pastes primarily consist of E-PVC with 50 to 65 % plasticizer or in exceptional cases 80 %. Here, the solvent, which initially serves as a processing auxiliary in which the PVC powder is dispersed, is later eliminated by being absorbed by the powder, where it then serves as a plasticizer. The procedure is already old and has hardly developed for 40 years though its significance for the market is enormous. The most important products are spread coating products. In this case the paste is applied to a substrate, textiles in most cases, by doctors. In this way tarpaulins, imitation leather, and so forth are produced (fig.12).

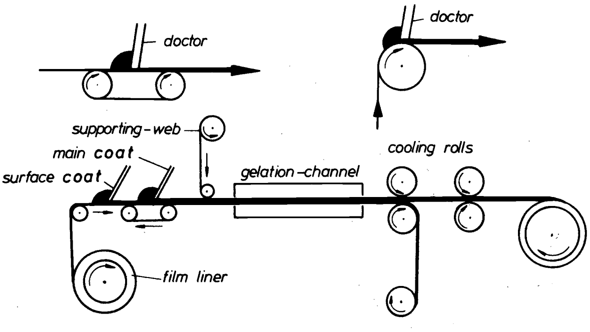


Figure 12: Spread coating procedure

This is also a question of the recipes which must be different for base, intermediate and top coats. After one coat has been applied it is gelled in a continuous heating furnace at 170 - 220°C. During this procedure the plasticizer is absorbed by the particles so that a dry plasticized PVC is produced after cooling.

During paste processing, too, the composition of the recipe must be adjusted exactly to the kind of processing, to the temperature in the gelling furnace and to the later application. The adjustment is effected through the choice of different kinds of PVC (particle structure and addition of B- and S-PVC which are difficult to paste) as well as the composition of the plasticizer as a mixture of differently structured plasticizers. Generally, these mixtures consist of non - polarizable groups - so-called shielding plasticizers on the one hand, and on the other hand of polarizable, so-called hinge plasticizers (21).
The complete gelling can be tested best - besides by a mechanical investigation - by a measurement of a direct - current resistance or by light transmittance by means of the acetic ester test (22). Ethyl acetate dissolves non-diffused plasticizer from the plasticized PVC during incorporation. During this process the cohesion between the particles is disturbed.

3. ATTEMPT TO INTERPRET THE ABNORMAL BEHAVIOUR OF PVC DURING PROCESSING

3.1 Present state of knowledge

Because of the abnormal flow behaviour of PVC Berens already supposed in 1967 that it was not a question of molecular sliding as otherwise during flowing of thermoplastic melts but a question of particle flow (23). The latest tests of flow- and elastic behaviour (26) on suspension PVC with K-values of

52 ($\bar{M}$ = 60 000)
61 ($\bar{M}$ = 110 000)
68 ($\bar{M}$ = 180 000)

confirm the older supposition in comparison with polystyrene and ABS. Fig. 13 shows the viscosities of these 3 materials. In contrast to polystyrene, PVC does not show Newtonian flow behaviour for low shear rates what can clearly be interpreted as "particle flow". The elastic behaviour, too, demonstrated by the elastic shear modulus (fig. 14) in comparison with ABS of different rubber (-particle) contents, shows that the PVC melt consists at least to a considerable extent of particles. However, it is remarkable that the flow behaviour and the elastic behaviour alter clearly at 200 - 210°C. The flow curves alter their gradient (fig. 15) at about 200 - 210°C.

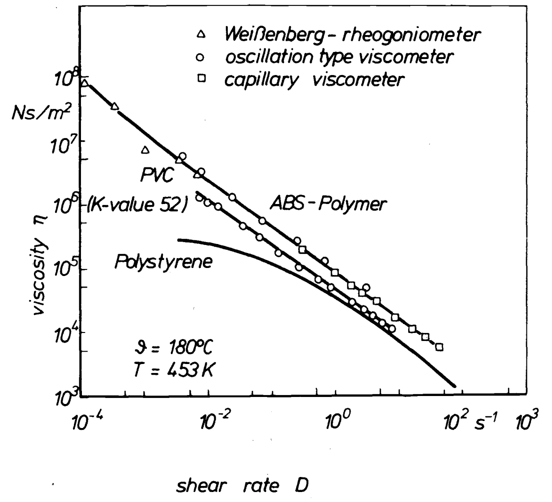


Figure 13: Viscosities of ABS, PVC and PS (according to (26))

Pezzin (34) achieved a similar result during the investigation of the flow behaviour of S-PVC. On this occasion, he ascertained a shifting of the break with the shear rate. While Pezzin attributes this shifting to the melting of crystallites in PVC, Münstedt concludes from electron microcopy investigations on ultra-thin slices which were carried out at the same time nondestructible or reversible particles exist. He speaks of "crosslinked" particles. Lyngaae-Jøgensen (37) also found crystalline areas in PVC which consist of 10 - 15 single molecules. This means that they probably measure 10 nm. So, they are in a considerably smaller order of magnitude than the particles described by other researchers, i.e. they form sub-structures. Contrary to the definition in macromolecular science the term "structure" is not meant in the sense of primary structure of the molecule chains but in the sense of super-molecular structure.

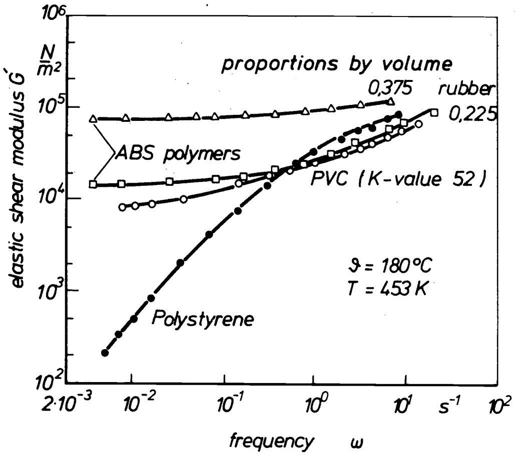


Figure 14: Modulus of shear of different plastics (according to Münstedt (26))

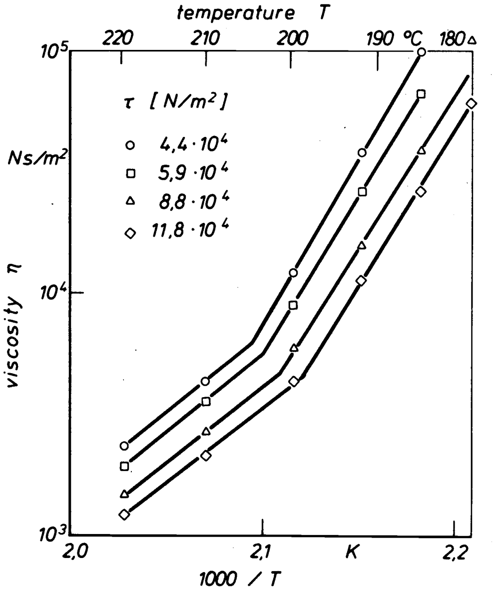


Figure 15: Viscosity of PVC as a function of temperature (Measurements of den Otter, quoted in (26))

The fact that the flow of PVC can be interpreted as particle flow has some essential consequences in practice. The swelling is unusually low and increases with temperature (34) in contrast to normal polymer melts as there arises almost a block flow on account of the particle flow during which only slight orientations occur in the material. This fact predestines PVC for the production of profiles, as is well-known.

Moreover, the flow behaviour is non-Newtonian as during the flowing a certain inter-surface tension between the particles must be exceeded before the latter slide against each other (34). The deformation of the particles seems to be very slight. So, in PVC-EVAC samples Kämpf (38) found that the structure does not change in elongated samples and that the deformation probably results from the sliding processes between the particles. Similar suppositions can be made in the case of the flowing of the melt.

Moreover, recent publications of P.H. Geil et al. (24) confirm again that the particles which arose during polymerization remained constant at 0.1 - 2 µm even in the case of plasticized PVC which had been mixed on rollers. However, in the case of higher plasticizer contents a "nodular" structure becomes more **apparent which is hundred-fold smaller. Geil et al. think that these nodules are the smallest structural unit which can still be** influenced by the processing method.

We ourselves found in high-impact and apparent straight rigid PVCs (pipe mixtures) which had been formed for the first time to profiles and foils by us as well as by others from S-, E- and B-PVC types, that in no case had the particle structure resulting from polymerization (0.1 - 2 µm) been caused to disappear (25). In contrast to most of our predecessors, we etch our samples with an argon ion beam in order to avoid any chemical influence. By using low pressure of 0.005 m bar we take care that melting does not occur. Only in one case when we found shear stresses of about 20.000 N/m^2 at 230°C melt temperature, almost structureless etchings were produced (29). It has not yet been possible for us to investigate plasticized PVC.

3.2 Morphology and strength

An essential property of PVC is the impact strength α_K which depends on the faults present in the material and thus on the critical strain ε_{F_∞}

$$\alpha_k = f\,(\varepsilon_{F_\infty})$$

$$\varepsilon_{F_\infty} \approx \sqrt{\frac{\gamma}{E^o\, a}}$$

γ = interfacial energy by which potentially weak points stick together

E^o = short-term modulus of the particles

a = diameter of the particles

Consequently, there are three possibilities for obtaining a high impact strength α_k:

1. Short-term modulus E^o. This occurs in the case of plasticized PVC; however, it can be used in practice only if the rigidity is still sufficient to support loads.

2. As small particles as possible, i.e. little a. This means the globules ought to be opened in order to obtain the nodules as the smallest structural unit.
   Thus all
      aggregates
      powder grains
      globules
   throughout the material must surely be destroyed during manufacture in all areas which are subject to positive strain. Moreover, there must not be any filler particles larger than the nodules themselves (< 100 nm). Up to now, this has been impossible because the necessary temperature and shear cannot be attained without decomposition in normal manufacturing plants. The globules are attained only as smallest particles.

3. Increase of the interfacial energy γ by interparticular "adhesive substances" (modifiers).

3.3 The capillary force system (25)

If obviously many factors point to the fact that the particles of 0.1 - 2 µm arising during polymerization - we called them globules - survive processing undestroyed, i.e. at most deformed, then the question as to the cohesiveness of the PVC material arises again. Here it cannot be a question of PVC macromolecules which are entwined with each other and which attract each other by strong side valence forces causing the cohesion in this way. At first sight it is scarcely credible that the recipe components could provide the adhesive for the globules. But physics provides a model which could also be considered. This is the mechanism which keeps moist sand together owing to capillary forces. Here fluid menisci have developed between the sand grains. The capillary forces p_k arising in the menisci permit the transmittance of considerable tensile stresses.

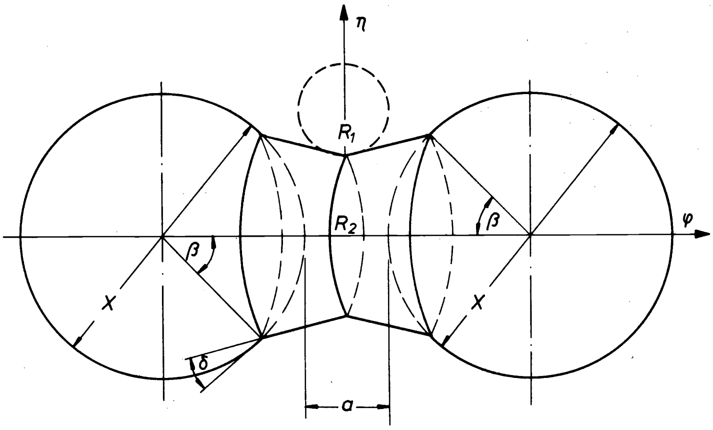


Figure 16: Fluid bridge between two spheres (30)

Thus $\sigma_B = S \times p_k$ where

S is the degree of saturation, i.e. that part of the total volume of the space between the particles which is filled with the meniscus fluid. In figure 17 the transmittable tensile stresses σ_B are shown for a sand/water mixture according to Schubert (30). It can be seen that the transmittable stress has a maximum with a degree of saturation by volume of

$$0.8 < S < 0.95$$

The capillary pressure can be measured relatively easily and works out at

$$p_k = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad \text{(see figure 16)}$$

The capillary pressure is very high if the surface tension of the meniscus fluid is high, too and if the radii R_1 and R_2 are small. The smaller the globules and the better the wetting the more favourable are the low capillary pressures arising.

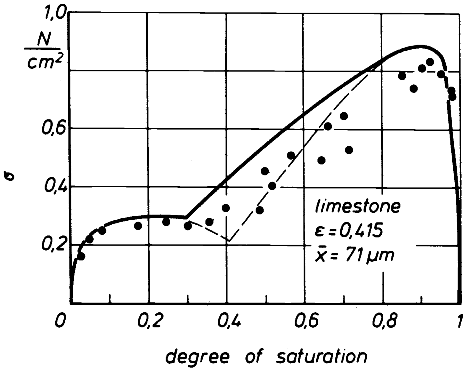


Figure 17: Maximum transmittable tensile stress in a moist heap of material (13).

Of course, it must be asked what the substance between the particles of PVC could be. It can be supposed that - beside the recipe "partners" the accompanying products of polymerization occur again here. Low molecular weight PVC molecules could also play a part.

This analogy is of course only a first approximation, because sand is built up of mainly isometric grains with a packing-volume-share of about 74 %, whereas with PVC the packing-volume-share will be about 80 - 90 % caused by deformation of the globules (compare with measurements of Demmler (39) at UP-resins).

This causes even greater capillary forces than with a packing of ideal spheres. Beside this the coupling of the interglobular material plays an important roll as it is known from mixtures of PVC and rubber. The resulting adhesive-forces are added to the capillary-forces (40).

This model is especially plausible for the explanation of the flowing and gelling of pastes, of course. As long as the volume of the fluid is in excess in the paste, i.e. above the degree of saturation of 100 %, only a low strength of plasticizer is given. Owing to diffusion between the grains during gelling and wetting of the globules with their very large surfaces in comparison with the grains, the dispersion dries down to degrees of saturation below 100 % and a considerably higher strength arises. As, according to the observations of Geil et al. (24), it must be supposed that the plasticizer also penetrates into the globules and there becomes embedded between the nodules. The globules themselves become softer, but without losing their cohesiveness. This would be a satisfactory explanation of the low elasticity modulus of plasticized PVC. But between the globules the rest of the recipe components remain as a putty substance together with the remainder of the plasticizer. This would **explain the high thoughness of plasticized PVC up to elevated temperatures. Only when the putty substance itself freezes at low temperatures does the bond become brittle.**

It is also well-known that the grains should be absolutely destroyed during the processing of rigid PVC (13,14). Only when the auxiliary materials, especially the stabilizers, are evenly attached to the globules, does the material have long-term light stability for example. So today, it is well-known from the observations of Menzel (31) and Trautvetter (28) that the way the additives are distributed is of decisive importance. Figure 18 shows electron micrographs(by von Bassewitz/Menzel (31)) of ultra-thin slices of high impact rigid PVC contrasted with OsO_4. Surprisingly, only that material in which the impact modifier surrounded the globules(fig. 18), i.e. where a reticular or alveolar structure had formed, proved to have a high impact strength.

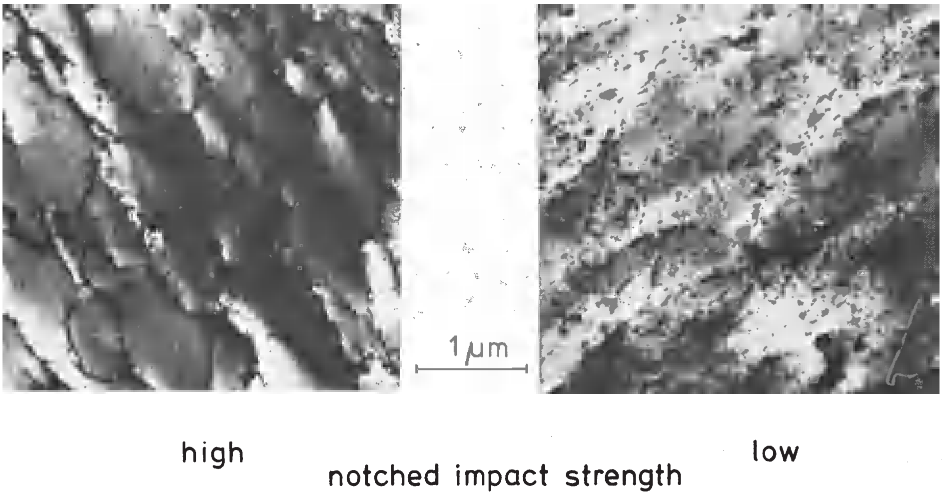


Figure 18: Photographs of the structure of PVC with high and low notched impact strength (according to von Bassewitz-Menzel (35)).

If processing at very high temperature was effected to the extent that the distribution was even over the cross-section, as in figure 18b, then the impact strength was largely lost. This means that the kind of processing must particulary be taken into consideration, as it has obviously more influence than the recipe itself.

That an alveolar distribution of the impact modifier (here: Levapren) in PVC is a precondition for a high notched impact strength is confirmed by investigations by Warmuth (36) who observed that during the extrusion of HI-PVC the highest possible notched impact strength can only be attained in a relatively small melt temperature range (fig. 19).

Kämpf (38) attained the same result with PVC-EVAC. The globular structure vanished at about $190^{\circ}C$ and at the same time the notch impact strength decreased from 37 kJ/m^2 to 5 kJ/m^2.

It must be added that it is impossible to indicate a fixed temperature at which this structure is developed to the optimum. The mechanical energy (shearing) must also be considered, thus an optimum processing temperature arises for one set of operating conditions (each throughput) and for the given screw geometry.

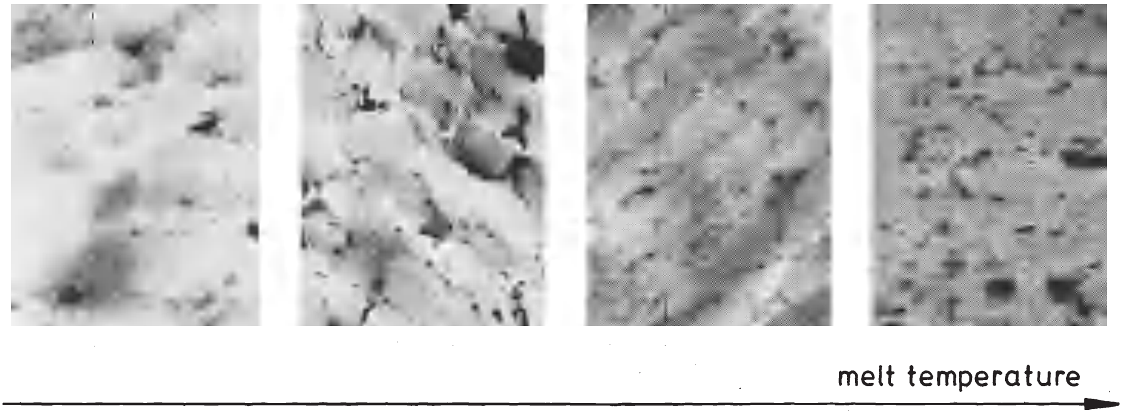


Figure 19: Structural change in HI-PVC with increase of the extrusion temperature (according to Warmuth/von Bassewitz (36)).

3.4 Conclusions and consequences

Our present knowledge about PVC can be summarized as follows:

1. The globules (0.1 - 2 μm) arising during polymerization remain undestroyed up to high temperatures (> 230°C in rigid PVC). At most they are deformed for better filling of cavities.
2. A sufficiently good product quality must guarantee the destruction of the raw material grains (about 100 μm) as well as an even distribution of the additives among the globules.
3. The globules are kept together by a "putty substance". A cohesive binding is probably no longer to be expected.
4. The "putty substance" consists of
   - residues of the polymerization auxiliaries
   - low-molecular weight PVC
   - the recipe components such as
     - lubricants
     - chelators
     - stabilizers
     - polymeric modifiers

   and in plasticized PVC: - parts of the plasticizer.

There is the following consequence for the choice of the recipe components:

5. They must have a high affinity with the surface of the globules (wetting).
6. It must be possible to mix them with each other and to increase the wetting capacity.
7. They must not diffuse into the globules - except for the plasticizer as otherwise ageing must be expected (such ageing is often observed even when the material is stored in a pure form.
8. The putty substance must be present in plastified form in the whole area of application and processing. It mut not undergo changes on processing.

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