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THE POLYMERIZATION, STRUCTURE AND PROPERTIES

OF BULK PCV IN CORRELATION WITH MOLECULAR WEIGHT

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In the fields of plastics, PVC occupies a predominant position on the world market, because of its exceptional properties and the large range of applications: one can say that there are no plastic conversion methods where it cannot be employed. This considerable success can be measured by the tonnage of PVC. World production exceeded 4 million metric tons in 1966 and it is forecasted that the annual increase will exceed 10%. In order to demonstrate this, it is sufficient to study the PVC consumption figures for the past 7 years.

tonnage in 1,000 t	1960	1964	1965	1966	1967
USA	424	734	833	999	946
America (excl. USA)	26	82	37	92	105
Asia	261	512	528	541	770
Western Europe	555	1195	1300	1437	1606
Eastern Europe	126	326	372	417	460
Other countries	0	11	12	14	13
Total	1492	2660	3130	3506	3900

The capacities forecasted in Western Europe for 1970 should be of the order of 2.300.000 metric tons per annum.

Historically, PVC resins were first produced as emulsions and suspensions and later in bulk by a process developed by Technicy-Saine-Gobain: in less than 2 years, more than 10% of the world production will be produced by the bulk process.

I Bulk Polymerisation

In the case of the emulsion process the monomer is dispersed in a immiscible medium, generally water, with the aid of a surface active agent (soap, alkylaryl sulfonate etc.) and in the presence of a catalyst soluble in water: the polymer is produced in the form of a stable latex of which the very fine particles (0,1 to 1 micron) cannot be filtered: the resin separation can be effected by means of drying the latex or by coagulation, filtration and drying.

But in all cases, resins suspended from the aqueous solution retain some of the emulsifier to a greater or lesser extent.

The suspension process works on the following principle: when the VC monomer, which is insoluble in water, is moderately stirred, it divides into fine droplets of various sizes depending on the rate or length of the agitation concerned. The polymerization of these droplets to resin occurs under influence of heat and of a catalyst which is soluble in the monomer. To stop coagulation of the droplets and to liberate them of the resin particles a colloid protective is added. The particles in the form of particles into a size range of 10 to 15 microns and are separated from the water by filtration and drying.

Both these processes use water which has the advantage of being an excellent heat transfer agent but the disadvantage of requiring filtration, drying or steam-heated evaporation process and the use of emulsifier, catalyst and colloid protectors (suspension process).

The bulk process entirely avoids the use of water.

Vinyl chloride lends itself particularly well to the bulk polymerization process by virtue of its physical characteristics (boiling point = 14°C , viscosity = 0.193 c.p.s. at 20°C).

The basic principle is as follows:

The polymer produced being insoluble in the monomer, precipitates to form grains which even with moderate agitation have no tendency to agglomerate. The reactors can, therefore, be agitated without difficulty.

As the polymerization temperature is generally between 40°C and 70°C , the monomer in the reactor is at a pressure of 5 to 10 lb./sq. in. The liquid monomer is constantly in equilibrium with its vapour and the heat of reaction can be easily removed by evaporation and condensation of the monomer. Similarly, the unreacted vinyl chloride monomer at the end of the polymerization can be easily eliminated.

We have been able to show that the polymerization of vinyl chloride is carried out in two distinct phases:

- a phase in which the polymer grains are formed and the final structure of the resin is pre-determined. This phase is virtually completed when 7 to 10% of the monomer has been polymerized.

- a phase in which the grains increase in size. This growth phase continues until 70 to 90 % of the vinyl chloride monomer has been polymerised.

During the grain forming period, it is essential to be able to agitate effectively the material in a liquid state and in a high degree of turbulence to obtain the required particle size distribution.

The greater the agitation the smaller the average grain size. It is also possible during the first period of polymerisation to vary the density of the grains and subsequently the bulk density of the final resin. This phase of the reaction is achieved in a vertical autoclave constructed of stainless steel which we call the "pre-polymeriser" and which is fitted with an agitator of the flat bladed turbine type and with baffles which prevent the formation of a vortex in this low viscosity medium. It has been shown that it is unnecessary for the total charge of vinyl chloride monomer to be pre-polymerised; half the charge is sufficient to provide the seeds from which resins of excellent characteristics are produced in the second reactor.

During the second polymerisation phase, the grains formed in the initial period grow. Once the concentration of polymer reaches 20 % there is practically no free monomer around the grains, and it is entirely absorbed by the grains which have grown previously. The polymerisation thereafter takes place in the solid powder and the equipment must be specially designed to suit. The autoclave is of horizontal construction in stainless steel equipped with a slow turning paddle-type agitator.

The conversion ratio of the monomer is established by the continuous computation of the quantity of heat released in the course of the reaction, on the premise that the polymerisation of 1 kg of vinyl chloride releases 370 Kcal. When the required value is achieved the unreacted monomer is degassed and the vinyl chloride monomer is recovered and reused without further treatment for subsequent polymerisation.

As duration of these two phases are entirely different, with the pre-polymerisation phase being approximately four times shorter than the polymerisation phase, it is possible for a single pre-polymeriser to serve several autoclaves.

(see chart. no. 1)

II The Structure of Bulk PVC

Because of the particular polymerisation process, the PVC grain from the bulk process has a very special structure. Let us try to explain the evolution of the grains in the course of polymerisation.

During the first polymerisation stage (from 0% to 1%) conversion of the monomer we observe the appearance of very small particles which progressively make the liquid medium more opaque. The particles consist of polymer chains which remain separate. Thereafter the concentration of elementary particles increases and we can observe the phenomenon of the association of these particles which gives birth to an elementary grain whose average dimension is of the order of 0.1 micron. The number of grains will not change further in the course of polymerisation whilst their average diameter will increase and reach approximately 0.9 to 1 micron once the conversion ratio reaches 80%.

During the further progress of polymerisation a second stage of association can be seen, this time consisting of an association of the granules which produces the final grains which are all formed when the conversion ratio reaches 2%. The number of grains, too, remain constant during the course of reaction.

A microscope enables the comparison to be made between the multi-cellular structure of the best suspension type PVCs (photo 1 and 2).

In the case of the suspension type, the structure is globular, that is to say separate cells form part of the basic grain.

If one increases the magnification one detects in the bulk PVC the agglomeration of granules corresponding to the evolution of the polymerisation described above (photo no. 3). These elementary granules have a diameter of about 0.5 to 1.5 micron and are highly friable on their surface.

Let us now compare bulk PVC with traditional PVC by high magnification microscopic examination. One sees (photo no. 4) that the structure of bulk PVC is at first sight comparable to that of a coagulated latex (opaque grains with ill defined contours).

III Fundamental Properties of Powders

Let us first of all try to define the fundamental characteristics of bulk PVC powders in relation to the structure that we have just considered. These

properties are evidently determining factors in the conversion of the powders:

- The morphological properties will affect the preparation of mixtures and the feed to the machines,
- The gelification and rheological properties will affect the conversion from the powder to the molten state.

As a first approximation, one can say that to each application corresponds an appropriate molecular weight. Also a large part of the results will be expressed in a function of the M_w/M_n ratio. In the next inter-actions of these different properties. As far as possible, we will endeavour to compare these results with those obtained from traditional suspension processes in order that they can be generally understood.

III 1 Morphological Properties

The bulk density, the sieve analysis, the porosity and the rate of absorption of the plasticizer will determine the flow properties of the resin: It is quite evident that the average diameter of the resin will be a very important factor: the higher it is, the greater is its flowability, but conversely the gelification conditions will be less good.

Therefore, for this lecture we will discuss a resin with a normal average diameter (110 to 130 microns) for both suspension and bulk resins. It is quite evident that, according to the application considered, this value of the average diameter will have a greater or lesser importance (extrusion and calendaring for example).

For clarity, we have assembled all these results in graphical form and we have chosen as points of comparison excellent suspension type resins produced in Europe.

Therefore, in particular, how do bulk resins compare with suspension resins?

- higher bulk densities (figure 1) which is very important for example for production rates in extrusion processes,
- higher porosities whatever the used (figure 2),
- saturation ratios for high percentage mixtures at variable temperature (figure 3).

- much higher absorption rates of plasticizer expressed in %/minute whichever system of plasticizing is used: PDC, DC or mixture of DC and chlorinated paraffin;
- narrow band of particle size distribution (figure 5).

All these properties lead to a superior flow, and a lower rate of gelation in PVC; this is due to the fact that such bulk PVC, no gelification takes place whilst in the case of suspension PVC, a colloid/colloid friction occurs (or plasticizer solution - colloid) depending on the nature of this ingredient (figure 6).

At equal bulk density, one notes that:

- the porosity is higher than that of suspension resins (figure 7),
- the speed of absorption of the plasticizer and the saturation ratio are higher than those of suspension resins (figure 8).

III 2 Properties concerning gelification.

We will attribute to the term gelification the basic definition that is the mass solidification of an amorphous form of an apparently homogeneous gel starting from a homogeneous material (i.e. powder or dry-blend).

Under the influence of temperature, pressure and/or time the grain structure of PVC will be destroyed and all the primary granules will adhere to each other resulting in a melt. For a given temperature, time will permit the formation of the material and the achievement of its mechanical properties.

To illustrate this applied to gelify we have compared as a function of molecular weights the time of gelification in rigid formulation (figure 9) and the gelification temperatures in plasticized formulation (figure 10) of bulk PVC and of a series of traditional suspension PVCs using a standard plastograph.

- The gelification time in rigid formulation is 20% to 30% lower for a bulk resin than for a suspension resin.
- The gelification temperature in plasticized formulation is 5° C to 10° C lower than for a suspension resin.

Let us add that in the absence of pressure the bulk PVC has very interesting

properties of emulsion as shown by the test results indicated by curve 11. All these results can be explained by the grain structure (porosity and absence of multicellular membranes) and by the very narrow band of particle size distribution. This last factor has not been properly examined as shown on curve no. 12.

In other words, bulk 20 should provide best compromise between bulk density/permeability characteristics and degree of stabilization.

III 3 Thermal stability

In the case of suspensions of bulk 20, the product is a colloid in the first case and the emulsion in the second case. It may be favourable or unfavourable depending on the method of stabilisation to be employed.

There exists a large number of tests to measure the thermal stability.

Reverdin test is of dynamic stability with continuous recycling on an extruder until complete burning of the product. Practical evaluation of thermal stability of emulsion in relation to method of stabilisation.

The industrial conversion of 20 is generally accompanied by the usage of 10 to 20% of the reactant in the process.

There exists other tests (static stability) using a press or an autoclave which also permit the evaluation of thermal stability of 20.

According to our tests there is a large difference in static stability between bulk 20 and suspension of 20. On the other hand with recycling tests on an extruder, the emulsion of bulk 20 prevents the internal friction and produces in some cases, better results.

We note that the specific weight of bulk 20 is lighter than that from the classical suspension type 20.

III 4 Properties of the finished product

The high purity of bulk 20 allows one to obtain in the finished product a remarkable transparency particularly useful in all applications concerning packaging.

The homogeneous characteristics of the grains of this resin allows one to avoid the problems of "fish-eye" which are so complex with the suspension type material (variable distribution of the colloids).

The absence of all chemical ingredients other than the catalyst permit one to avoid the problems of water absorption which may play a large role in the quality of tubes. We have only shown results obtained from cleaned and dried resins but it may be noted that the high degree of variability of the process allows one to obtain sufficient quantities of the chemical properties mentioned earlier as particular:

- the porosity can be increased or proportionately reduced (directed for patients),
- the tube diameter can be defined,
- the average diameter can be adjusted for the various applications.

IV Composing

All the fundamental properties of bulk resin that we have needed have great importance in an advanced application. The present practical applications and for each a large number of machines and therefore the principal quality of the bulk resin is its variability of composition. To obtain this fundamental quality, we have well known, for example, and we have decided to introduce of resin resin.

IV 1 Variability in the Composition of Bulk Resin

We have compared two different resins produced from two resins of the same bulk density (0.6). The first is a comparison resin whose porosity (5) is found to be a high bulk density (it is difficult, almost impossible, to obtain a higher porosity in the region of this density with the standard process).

The second is a bulk resin of a bulk density and of porosity which is quite normal for a bulk resin. These two resins have been tested in the following correlations:

Resin	100
Calcium stearate	1.5
Lubricant	7

The first part of the test consists of varying the proportion of lubricant at constant flow.

Taking the critical property, elongation for example, we examine the variation of this property in relation to the percentage of lubricant.

The curve is shown in the following figure:

From this curve it can be seen that in order to obtain good properties and to avoid the risk of fracture, the amount of lubricant must be expressed as a percentage of the weight of the material.

Supporting data: $\frac{100}{100} = 1.0$
Bulk mass: $\frac{100}{100} = 1.0$

Now, if we use a low value for the amount of lubricant, the amount of lubricant is small.

It is possible to find a certain limit corresponding to acceptable mechanical properties for a given alloy.

3 standard deviations $\frac{100}{100} = 1.0$
Bulk mass $\frac{100}{100} = 1.0$

Instead of using a certain amount of lubricant, let us examine the effect of the amount of lubricant on the properties of the bulk product. The amount of lubricant is expressed as a percentage of the weight of the material. The amount of lubricant is expressed as a percentage of the weight of the material. The amount of lubricant is expressed as a percentage of the weight of the material.

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IV 2 Practical

All operations must be carried out in a controlled and steady operation.

From the above it can be seen that the amount of lubricant is expressed as a percentage of the weight of the material. The amount of lubricant is expressed as a percentage of the weight of the material. The amount of lubricant is expressed as a percentage of the weight of the material.

- the drying rate, whether mixed cold or mixed hot will be less than that with traditional drying processes.

and that in the convenience of material for field applications,

- the dust should be finely divided, non-clumping and the additives will permit the use of a wide range of equipment,
- the dust should be of a size which will allow greater flows to be obtained than with the present material.

IV 3 Conclusions

It was concluded that there were important differences between the two types of material for field applications, differences having to do with the ease of application, the quality of the finished product,

the cost of the material and the ease of application in practical applications.

References

In the course of the investigation it was particularly vividly recalled that the dust should be of a size which will allow greater flows to be obtained than with the present material. It was also noted that the dust should be of a size which will allow greater flows to be obtained than with the present material. It was also noted that the dust should be of a size which will allow greater flows to be obtained than with the present material.

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Conclusions

The two types of material are of a similar type of application and

- the dust should be of a size which will allow greater flows to be obtained than with the present material.
 - the dust should be of a size which will allow greater flows to be obtained than with the present material.
- quantities of material used in the preparation of the material. It was also noted that the dust should be of a size which will allow greater flows to be obtained than with the present material.

ween bulk PVC and a good suspension PVC.

These curves illustrate the great versatility which allows a high amount of plasticizer to be

Furthermore, in all series of this type, the plasticizer content can be considered, for present, technical suspension PVC.

Let us add first as a consequence of the reaction the bulk PVC is practically free of "fish-

In plasticized extrusions, its use of gel is relatively low, several temperatures and the favourable compression, a much productivity and quality.

In plasticized injection moulding, its use of high molecular weight resins.

In calendaring, the fundamental gelification mixer located upstream of the press. It is possible the cyclization of the mixer.

May be added that films with a very fine texture easily be obtained by this method of conversion.

It is quite evident that in all these applications where a high degree of transparency is required, properties, which are not better than those obtained with suspension applications such as coating.

In conclusion, bulk PVC shows in relation great differences in structure and morphology conditions, a manufacturing facility of high order qualities, leading to a very interesting product.

In addition, this product, in the state of a large range in the basic characteristics of the

line and composition can be used as well with emulsion resins. They also have the technique the viscosity of plastic to improve, requiring other

Very porous resins (in the form of dry bl