

THE MORPHOLOGY, RHEOLOGY AND PROCESSING PROPERTIES OF POLYVINYL CHLORIDE

C. L. Sieglaff

Diamond Shamrock Corporation, P.O. Box 348, Painesville, OH 44077

Abstract - The critical observations of Berens and Folt (1) and Collins and Kriër (2) have focused research on the particulate nature of PVC. It has been shown by many working in the field that this particulate nature is the controlling feature in both the fusion and flow behavior of PVC compounds. The morphological nature of the suspension resin can be related to the ease of processing of PVC compounds. Resin particles with interior particulate material loosely packed break apart easily and are more readily processed than tightly packed systems. Resin particle uniformity is also important in the fusion process. A model for the fusion process of PVC is proposed based upon these findings. The effects of additives used in compounds is discussed. The factors the author views as being important for the future development of PVC processing is presented.

Polyvinyl chloride is the world's second largest commercial polymer and one of the oldest. Surprisingly, the work that has been done characterizing its rheological, morphological and physical properties has only taken place in the last two decades. The other major polymers such as polystyrenes and polyolefins, technical history goes back at least three or four decades. The reasons for this delay in the technical investigations of PVC was most likely due to the unique and complex properties of this polymer. In addition to the complex properties of PVC, a second major drawback to its study is its thermal degradation properties.

What I will do in this presentation is to present a brief overview of the last two decades of scientific work on PVC, then a summary of the present work that is being done, and lastly, I will summarize what I feel are the areas of future research in the rheological and processing properties of PVC.

In the early 1960's, those of us who were working determining the melt flow properties of PVC, essentially were treating PVC as a normal homogeneous polymer melt (1-5). Results usually were presented in the form of flow curves (Fig. 1).

FLOW CURVES FOR PVC-450

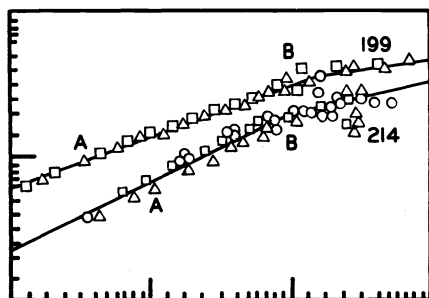


Fig. 1 Flow curves for PVC

GEON RESIN, IOIEP F 24

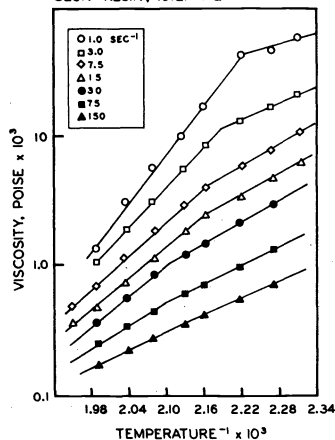


Fig. 2 Collins Viscosity vs Temperature

These compounds or polymer systems were normally prepared by milling the polymer and then compression molding the material into suitable samples for the rheometers used at that time. This approach of milling and molding was done in order to obtain so-called reproducible samples and to give reproducible results. We observed the normal melt behavior of a polymer in the study of these systems. The elastic irregularities present in polymer flow were observed, such as the shark skin and melt fracture. We also observed the die swell behavior that is typical of polymer melts. The one piece of data that was reported at that time, that was not understood, which I think we can now explain, was the effect of temperature on die swell (3). At that time it was reported that the die swell increased with temperature, which was not typical of other polymers. Normally, the die swell would decrease with increasing temperature.

In the late 1960's, Berens & Folt published their now historic paper on the particulate nature of PVC melts (6). In their original work, Berens and Folt were studying emulsion polymers, but in a later paper, they extended the particulate nature to suspension polymers (8,9). Shortly after Berens' paper was published, Collins and Krier (7) published an analysis of the temperature dependence of the flow properties of PVC. In this landmark paper, Collins and Krier pointed out that there was a transition in the flow unit in PVC that occurred at approximately 200°C. This paper sent us all back to examining our previous data and looking at it not as an experimental error or experimental difficulty, but looking at it in terms of a change in flow mechanism. Figure (2) shows some data that we had originally published as a linear plot, but Collins' paper, definitely showed there was a change in flow mechanism. More detailed study of these polymers systems showed that at a low temperature, the viscosity could actually increase as one increased the temperature, rather than the expected decrease as shown in Figure (3). These two papers, the Berens and Folt paper and the Collins and Krier paper, opened up a whole new avenue and a completely new approach to the study of PVC melts. Up to this point in time, we were considering PVC melts as a homogeneous system and trying to explain its behavior on the basis of a homogeneous entanglement network without too much success. The advent of the viewing of PVC melts as a heterogeneous supermolecular structured material, allowed us to have a better insight into the behavior of PVC. The decade of the 70's has been primarily devoted to studying the origins of this particulate structure within the PVC melt.

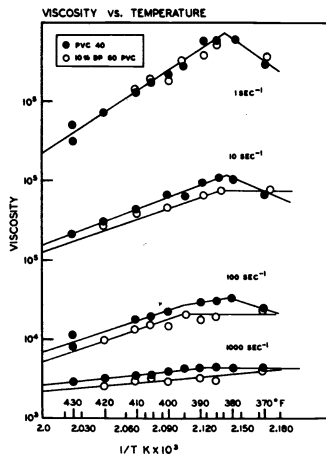


Fig. 3 Replot of η vs $1/T$

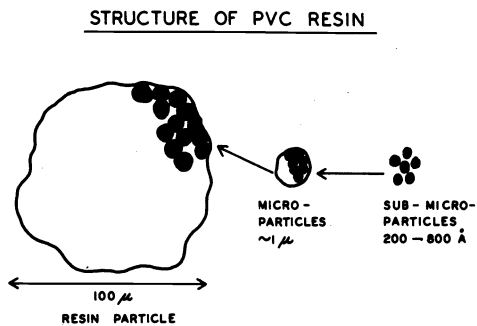
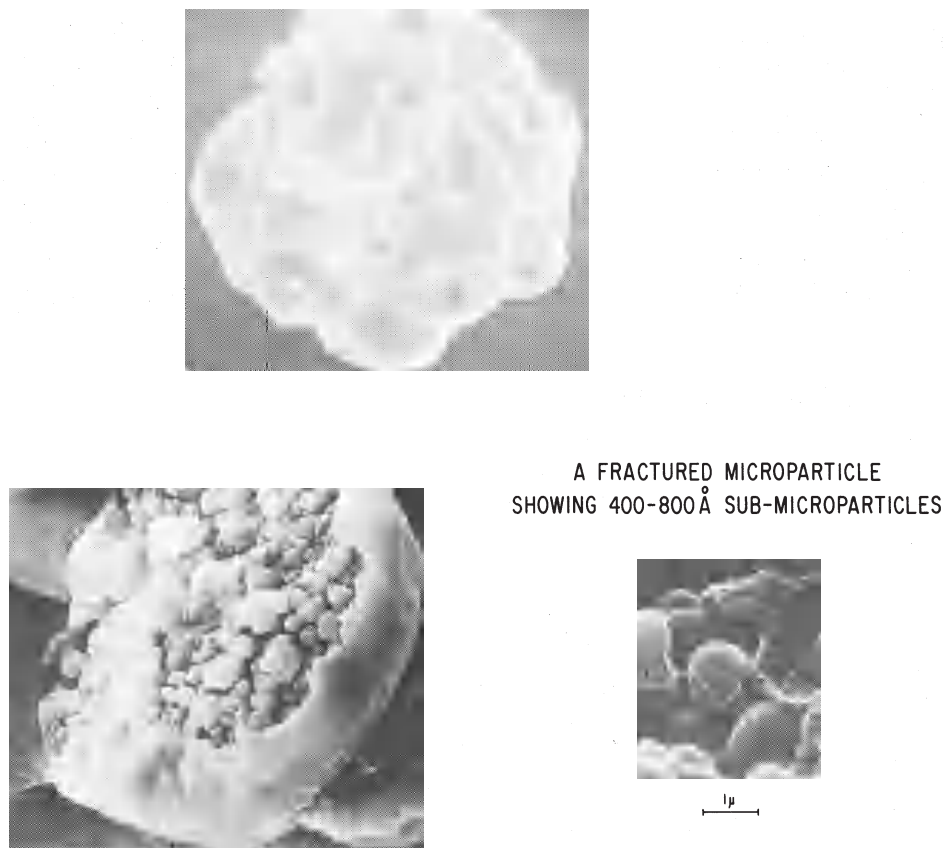


Fig. 4 Schematic structure of PVC particle

Figure (4) is a schematic diagram as we now perceive the PVC particulate structure. The accepted view for PVC suspension resin structure is a 100 to 200 micron particle, made up itself of agglomerates of particles from 20 to 50 microns (27). Within the large resin particle, there are microparticles of an order of magnitude of 1 to 2 microns. These, in turn, are composed of submicroparticles of the order magnitude of 100 to 1000 Å. Figure (5) is a picture of a typical PVC suspension particle, the exterior being a prune-like surface, obviously formed by agglomeration of smaller particles. This particular resin particle, has a break in the skin through which one can see the micron particles. Figure (6) is a better view of the interior of a fractured PVC particle, showing the microparticles and also the skin, a pericellular membrane. Figure (7) is a fractured PVC particle in which one of the microparticles has fractured showing again the skin about this particle, the interior is composed of very small angstrom sized submicroparticles. These submicroparticles measure about 400 to 800 Å.



A FRACTURED MICROPARTICLE
SHOWING 400-800 Å SUB-MICROPARTICLES

Fig. 5, 6, and 7 PVC Suspension particle in progressive states of breakdown.

The network structure that processing develops within these small grains plays a profound role in rheology, processing and indeed the ultimate properties of the finished material. The key to having a PVC that processes well and performs well, by in large, lies in the understanding of this particulate structure, and is coupled with the understanding of the particulate structure in its role in the fusion process.

PVC is a semicrystalline material. This in itself is not unusual. However, the crystallinity is difficult to measure and varies considerably with the conditions under which it is produced and varies also with the process history of the material. The high crystalline melting point, of the order of 260°C, dictates the PVC is almost always processed below the crystalline melting point. This alone presents unusual properties and processing behavior problems. It should be mentioned that PVC has a broad range of crystalline melting points. The running of repetitive thermal cycles produces crystals that melt at progressively higher and higher temperatures. The range of melting points that have been reported start at approximately 120°C and proceed as stated before to 260°C. Each thermal cycle that the PVC sees changes this range toward higher temperatures. In this regard, working or reworking PVC is like working with a new material each time. This role of crystallinity in the processing and ultimate properties of PVC, is still under intensive investigation and is not yet to the point of total understanding.

With this background of the scientific advances in the 60's, we move into the 70's. During this period of time, the primary efforts in the study of the rheological and processing properties of PVC, centered on the description of mechanism of the fusion or gelation properties of PVC resins. Gonze (2) and Lamberty (14) published a methodology of determining the degree of fusion of a processed PVC resin. This methodology essentially measures the elastic pressure loss at the entry of a capillary. By measuring the pressure losses in a short capillary at low temperatures, one is able to get a qualitative measurement of the elastic buildup in the processed PVC. First, one assumes the changes in the particulate structure can be assessed by corresponding changes in the elastic nature of the material. Second, with increasing degree of interpenetration of the particulate domains, the melt elasticity increases. And third, changes in the melt elasticity can be characterized by

changes in the capillary entrance pressure loss. This methodology is an indirect method and reflects the degree or extent of fusion of the resin materials. Direct morphological evidence can be obtained by microscopic evaluation of a processed resin. The PVC fusion process is a multistep process. The first step we have observed in both Brabender and extruder studies, is the breakdown of the resin particles, followed by a compaction of the broken particles (31). Sintering and interdiffusion is the third step of the process, both sintering of the micro and submicroparticles. Interparticle strength is developed and is the main factor determining the strength of fused materials. We used a temperature of 140°C with a capillary of diameter 1.6 mm with a length of 0.38 mm. This gives a L over D of 0.24 for our flat entry die. The measurements were made at a shear rate of 6 seconds (-1). The measured variable was the pressure to achieve this flow rate. Using a temperature programmed Brabender (24), we obtained samples sheared at different temperatures.

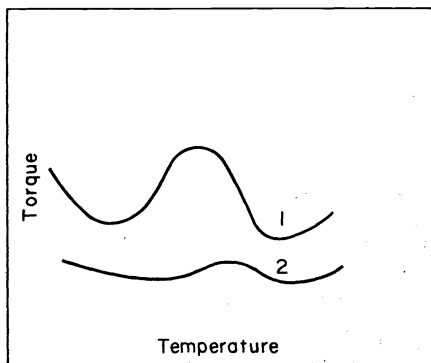


Fig. 8 Brabender torque curves

Figure (8) shows schematic Brabender torque curves as a function of temperature for two types of compounds; (1) a very simple compound containing stabilizer and a low level lubricant and (2) - a fully commercial compound. By taking samples at different temperatures and measuring the entry pressure loss in the rheometer, we're able to develop a fusion curve for these two compounds. Figure (9) shows these curves.

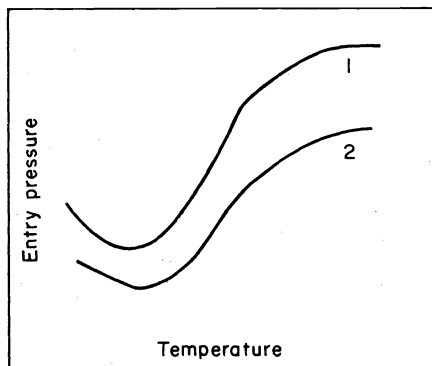


Fig. 9. Entry pressure loss vs temperature

As you can see, both compounds undergo first a drop in the pressure, which due to a decrease in the particle size of the resin, followed by an increasing pressure loss in the capillary entry. At approximately 200°C both compounds achieve a plateau in the entry pressure loss data. It is apparent from the curve, the absolute level of the entry pressure is dependent upon the formulation. As stated before, this sort of measurement of

fusion is indirect. The only direct method now available for measuring fusion or determining the state of fusion is optical observation of a material after it has undergone a shear-temperature history. Figure (10) is a photomicrograph of material pulled from the Brabender at 120°C the maximum in the Brabender torque curve. As can be seen from the picture, the primary resin particles have broken up leaving the micron sized particles in a state of loose compaction.

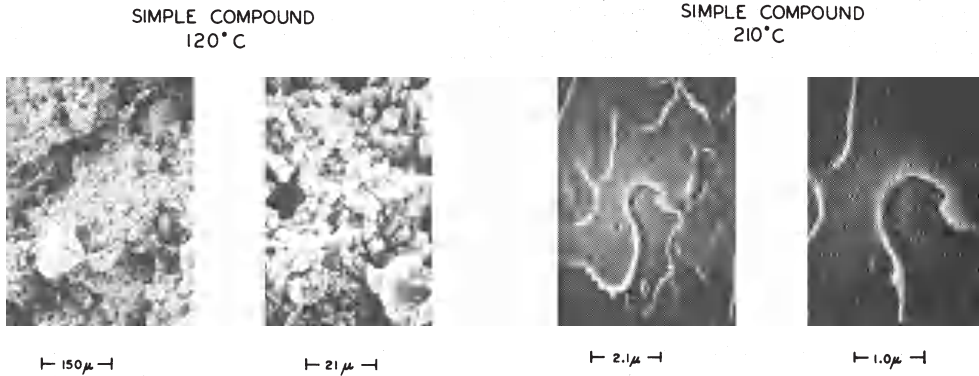


Fig. 10 Simple Compound at 120°C

Fig. 11 Simple Compound at 210°C

COMMERCIAL COMPOUND
180°C

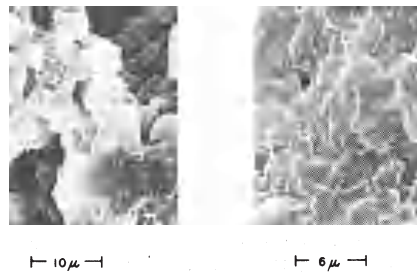


Fig. 12 Commercial Compound at 180°C

Figure (11) is the material from the simple compound at 210°C. At this magnification, there is no structure visible and appears as if we have a totally fused homogeneous material. The commercial compound even at 180°C does not appear to have broken up the one micron sized particles as shown on Fig. (12). As you can see, the particles have started to interparticle diffuse, but the structure of the individual particles is still visible. At 220°C the commercial compound again appears like the simple compound at 210°C, a uniformly fused appearing material.

As we saw, the fusion curve of two compounds do not necessarily have the same starting point in this fusion test, nor do they have same plateau region. But one can treat this data by reducing to zero percent at starting and to 100% at the final fusion plateau (32). If one looks at reduced data, one obtains a relative fusion curve. The difference in the rate of fusion is then clearly distinguishable between the two compounds.

SIMPLE COMPOUNDS
COMPRESSED AT 200°C

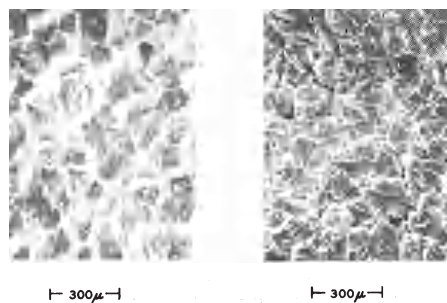


Fig. 13 Compounds Compressed at 200°C

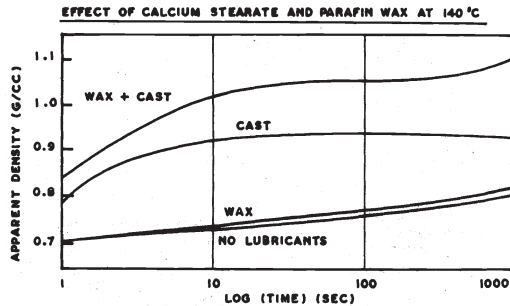


Fig. 14 Compaction vs time curves

These materials processed in a Brabender, experience both a shear and a compression process, but if one just compresses the compound without shear at 200°C, one achieves compaction as shown in Figure (14). Under simple compression without shear, the original particle nature is still observable (33). There is inter-particle diffusion between the original resin particles, but the structure is still definitely present. We have developed a method of measuring the density of compacted powder as a function of time at constant temperature. Figure (15) shows a plot of the apparent density of the powder as a function of log time for four different powder compounds. These data were obtained at 140°C and 7 kg/cm² pressure. The lower two curves, one containing no lubricants and one containing one phr wax, show a very gradually increasing compaction with time up to approximately 1000 seconds. The compound containing wax plus calcium stearate, on the other hand, shows a rather rapid rise in the density approaching the plateau region at about 10 seconds and then at about 1000 seconds again compacting somewhat further. Figure 16 shows the effects of temperature on the compaction rate of a powder compound containing the calcium stearate and wax. As can be seen as one raises the temperature of the material at a constant pressure of 7 kg/cm², the powder compacts to a higher density. At the low temperature, the compaction is limited to a fairly low apparent bulk density. At approximately 160°C compaction over long periods of time approaches the limiting density of the material, approximately 1.3. At 200°C one sees a rapid rise in the density approaching the plateau density of 1.3 in less than 100 seconds. The next series of figures are materials taken from the compaction tester at different times. The first Fig. (17) is for the material containing just wax at 10 seconds. As you can see, the original nature of the resin particles has not been distorted. Even at 1000 seconds, the material at a 180°C has not been distorted. The next photograph (18) is the wax and calcium stearate sample at 10 seconds and again we see little or no distortion of the resin particles at this time and pressure.

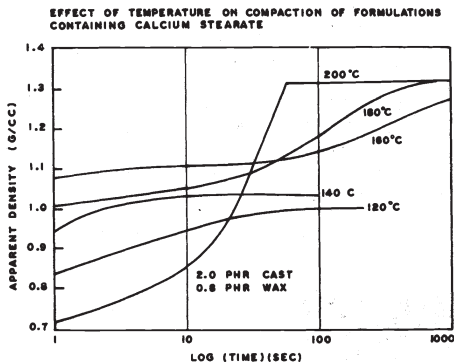


Fig. 15 Compaction vs Temp.



Fig. 16 Compacted Wax compound for 10 s.

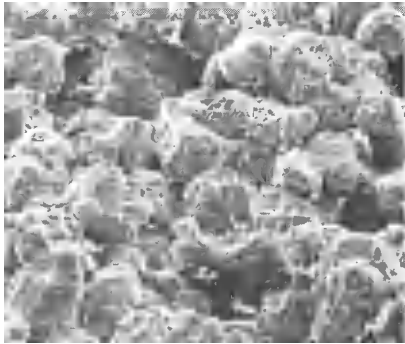


Fig. 17 Ten second compaction Wax and Ca Stearate

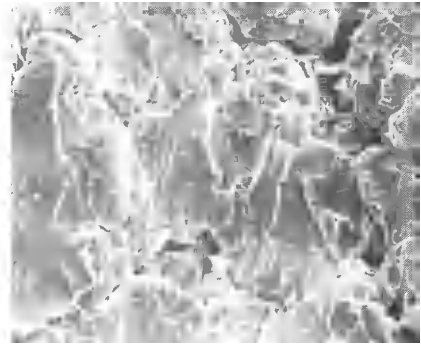


Fig. 18 1000 sec. compaction

At 1000 seconds Fig. (19), the particle exterior skeleton still is in evidence, but the interior of the particle has undergone a fusion process flattening out the resin particles. The last figure (20) in this series shows a compound that has been compacted at 160°C, but now at a pressure of 21 kg/sq cm, three times the pressure of the previous slides. At this temperature and this pressure, one can see that there is initiation of the fusion between the particles. In order to achieve this state of fusion, it was necessary to hold this sample under temperature and pressure for a total of 10 minutes. We're thus able to conclude that in a suspension PVC resin particle, shear is an important component in the breakdown of the original PVC grain into the micron size particles. This step is essential in the subsequent fusion of the PVC resin. It is reasonably clear that there are several different paths that fusion can take. Fusion can occur between particle grains under correct temperature pressure and shear conditions, and also fusion can occur within the grain particle, or it can occur within the one micron particles before having inner particle fusion. The overall picture that we have of the PVC suspension fusion process is three possible routes to a fused material. One route you have a breakdown of the particle to the submicron particles, the compaction of the submicron particles and interdiffusion to form a fused material. A second route is breakdown of the resin particles into the micron particles. These are compacted and internally fused or the particles themselves form a fused material. The third mechanism is no breakdown, but by compaction, temperature and long-time you get internal fusion of the resin particles and interdiffusion to form a fused material. This latter mechanism is limited by the thermal stability of the resin particles and the stabilizer content. Most likely, in commercial processing of PVC compounds, a combination of all three fusion processes has taken place. Definitive experiments have not been carried out which permits an unequivocal assessment of which process is predominant or which is desired and under what conditions they occur. The effective resin parameters, e.g., resin porosity, morphology, skin thickness, etc., have not been determined. The fusion route or the role of compounds additives in this fusion process, also have not been definitely determined. Continued experiments using the techniques of the entry pressure loss, coupled with morphological measurements and alternate property measurements will no doubt have many surprises in store for us in the future.



Fig. 19 Compaction at press. and temp.

INTERNAL STRUCTURE OF PVC PARTICLES

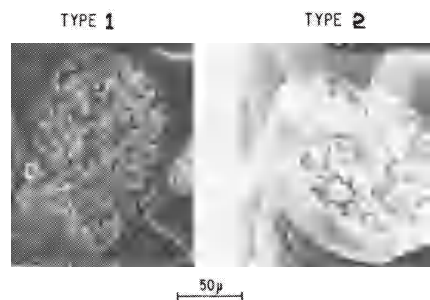


Fig. 20 Type 1 and 2 resin particles

A basic assumption that we have been making in this discussion is the existence of a fairly uniform PVC resin particle. Unfortunately, this is not the case, even in bulk polymerized PVC resin. We have done rather extensive studies on the particulate homogeneity of PVC resins with an emphasis on the suspension resin particle (27). In our microscopic studies we have been able to identify five structures within these PVC particles. Figure (21) shows micrographs of particles that have been fractured. The structure of the polymer particle on the left (type 1) is the rather open structure, loosely agglomerated 1 micron spherical particles. The one on the right is a somewhat tighter bound, and has tighter compaction of the 1 micron particles, resulting in lower porosity. In both of these pictures it is very clear that there is a rather sizeable membrane surrounding the interior structure of the PVC particles. These, I think, are exceptional pictures of this membrane. The next Fig. (22) shows an internal structure, that we've classified as a type 3 particle. In this case, the interior of the particle is very tightly packed and has a much lower porosity. The next Fig. (23) shows type 4 and 5 particles. The particle on the left hand side (type 4) contains a rather large void with somewhat loosely packed 1 micron material surrounding it. On the right hand side, the last type, is a particle that seems to be made up of two types of packing. The right hand side of the particle, is a loosely packed particulate structure, on the left hand side of the particle, there is a more tight and less porous structure.

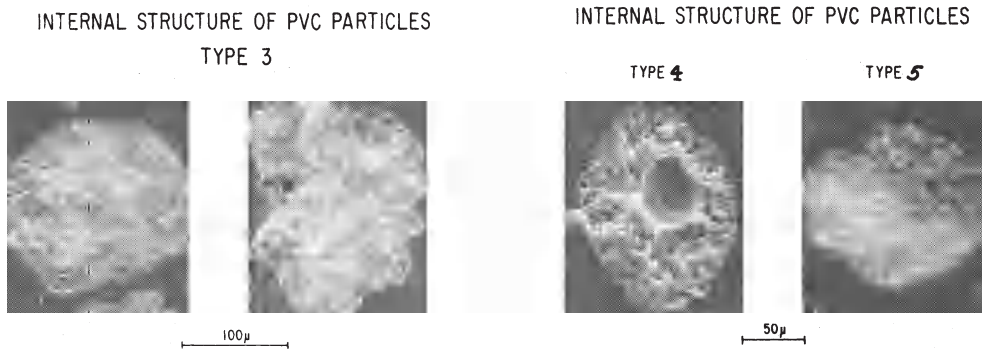


Fig. 21 Type 3 particles

Fig. 22 Type 4 and 5 particles

With this obvious heterogeneity of types of particles produced by the suspension process, it is obvious that a methodology which quantitatively determines the degree of porosity or degree of heterogeneity in a given resin would be of value to the PVC technologists. One of the methods that has been developed, is an adsorption of a fluid which will tend to make the interior of the resin particles more visible. Those particles which do not adsorb liquid or at a slow rate, appear to be opaque and without change when immersed in a wetting liquid. We also have developed a method of evaluating resin by an immersion technique. In this technique we immerse in a low molecular weight, low viscosity silicone oil. Figure (24) shows five different resins which have been immersed in this silicone oil for two hours. It is obvious that looking at these five different resins that as one goes from A to E in the resin series, one goes from fairly uniform porosity to a low porosity or impervious type resin particle. The intermediate samples show a mixture of the two types of particles. These methods have a weakness in that they only measure an average porosity for the resin system. As we saw in the last slide, there is a rather broad range of heterogeneity within a given resin sample. And an average may not be meaningful.

In order to alleviate this averaging problem within the porosity measurements, we have developed a further test to measure porosity of PVC resins (27). Simply described this is a density gradient technique in which we suspended PVC resin particles in fluids of different densities. The fluids were methanol-chloroform mixtures, which wet, but do not swell the resin particles. By measuring the quantity of material which floated or sank in these various liquids we could measure relative distribution of densities of the PVC particles. An assumption that is made was those pores within the particle, which were readily assessable to the liquid, would fill with liquid and those pores not assessable to the liquid would remain as voids, lowering the density of the particle. Figure (25) is density distribution curves obtained in this manner for the five resins that we looked at in the oil immersion system. Again, one can see that sample A essentially had no material that floated, it had a higher density than the solution until we got to a solution density of approximately 1.4. This indicated that the porosity is fairly uniform and was readily accessible to the liquids. On the other hand, sample E, the other extreme, showed a large number of particles that were not penetrated by the fluid and, hence, floated on the liquid, even at a density as low as 1.25.

PENETRATION BY SILICONE OIL
AFTER 2 HOURS

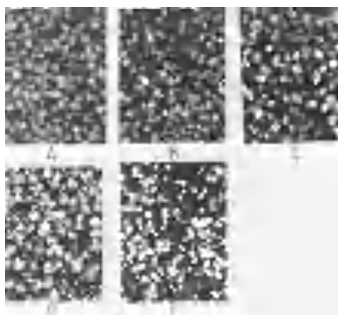


Fig. 23 Oil immersion of 5 resin samples

DENSITY DISTRIBUTION CURVES
RESINS A,B,C,D,E

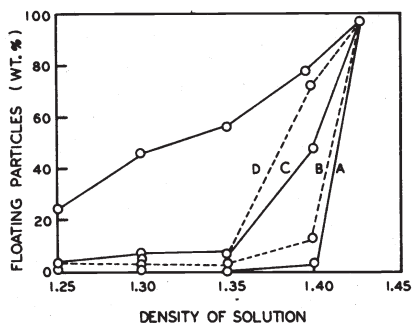


Fig. 24 Density distribution of resin samples

One can further analyze these types of distribution curves by trying to characterize porous types. On the next figure (26) we show homogeneity characterization for four of the five resins. By looking at percentages, we're able to show that the uniformity or heterogeneity of these resins were quite different and could characterize their porosity, and relate this variable to processing and processing properties. Figure (27) shows the results of extrusions of a homogeneous and a heterogeneous resin compounded in a pipe formulation. The experiment was a study varying the processing conditions for the two compounds and measuring the resulting impact strength of the pipe. As is apparent, the homogeneous resin produced pipe with good impact over the 70°F temperature range where the heterogeneous resin required higher temperature to achieve equivalent impact strength. We have concluded from a series of these studies that homogeneous porous structured resins can lead to more easily processed compounds due to their broader processing latitude.

RELATIVE AMOUNT OF PARTICLES
WITH DIFFERENT INTERNAL STRUCTURES

RESIN	INTERNAL STRUCTURE		
	VERY POROUS TYPE 1 AND 4	LESS POROUS TYPE 3	MIXED TYPE 5
A	~100%	~0%	0%
B	63	12	25*
C	62	25	13*
E	17	54	30+

* IN MOST PARTICLES THE VERY POROUS PORTION PREDOMINATES
+ IN MOST PARTICLES THE LESS POROUS PORTION PREDOMINATES

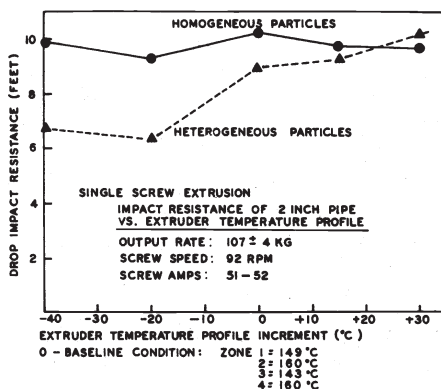


Fig. 25 Homogeneity of resin samples Fig. 26 Extrusion Characteristic of resins

In the study of PVC and PVC compounds, one can only use as a limiting case the resin properties themselves. In actual practice, PVC is never processed as a straight polymer, i.e., it is always processed in combination with several other ingredients. In discussing the processing properties of PVC, one must then also discuss the function of the additives, in particular, lubricants, processing aids, stabilizers, and even perhaps, plasticizers. It is well known that lubricants are primarily added to PVC resin to decrease the temperature and fusion rate of the PVC compound. These materials delay the buildup of heat by decreasing the viscous and frictional input of heat. At the same time they delay the heat input, they also are delaying the fusion process itself. It is agreed that the primary function of the lubricant takes place at the interface between the particles and the metal surface or between particle-particle. Recently, Chung and co-workers (25) have shown that

the coefficient of friction of PVC compounds was changed considerably with addition of lubricants. Unfortunately, we still need to be able to incorporate this into a mechanism of effective lubrication and understand the role the lubricants play in the fusion process.

Chauffoureaux (26) has shown that there is a direct relationship between the lubricant and the lubricant package on the flow and the flow mechanism in the die itself. His extensive and careful studies of the flow profiles and flow velocities in a die have shown a definite slip at the die wall which is a function of lubricants and temperature of the material in the die. Chauffoureaux has hypothesized that the role of the lubricant is diffusion of the lubricant to the wall with displacement of the PVC from the wall area. Slip is due to the shear of the lubricant layer itself. The lubricant's exact role will have to be understood in order to design a better compounding package for PVC resins and to be able to produce better degrees of processability.

We can discuss the additives that are used in PVC compounds separately, but it must be stated and emphasized that these additives do not act independent of each other. In commercial practice, one has to look at the additives package as a whole, it is necessary to balance these carefully. In particular, you must take care balancing the stabilizer-lubricant package. Processing aids are another common additive in a PVC compound. These materials are extremely interesting, although the mechanism by which they function is not totally understood. Generally, processing aids have a fairly high glass transition temperature relative to PVC, but at the same time, they have a lower tack temperature. The tack temperature is defined as the temperature at which the material has a viscosity of 10⁶ poise. This is the viscosity level where the material will either stick to itself or where intermolecular diffusion can occur. It is believed that the operating principal of a processing aid, is that it becomes tacky at a lower temperature than the PVC, and hence, functions as glue or heat transfer media for the PVC, initiating fusion of PVC. We surmise that the major function of the processing aid is to speed up the fusion or to initiate the fusion of the PVC. Now it is rather obvious that if we add a processing aid to speed up fusion and we add a lubricant to delay fusion, that we are essentially trying to compensate the action of the two additives. A good balance between processing aid and the lubricant is imperative so that one compensates for the other in addition to serving its own intended purpose. In many ways, small amounts of plasticizing additives behave similar to processing aids. A plasticizing additive does lower the temperature which fusion can take place, thereby increasing the rate fusion of the PVC resin. Often stabilizers themselves are plasticizers or they contain small amounts of plasticizers and can function in the capacity as a processing aid.

At this point, we have only briefly touched upon the molecular properties of the PVC molecule. By comparing PVC to other polymers, one finds major differences in the molecular properties of the polymer molecule. If one compares PVC to a polyethylene of about the same weight average molecular weight, it is found that PVC at low shear rates has a melt viscosity three times the viscosity of the polyethylene. Other polymers do not show this large a difference in melt flow behavior. This difference in the molecular properties is certainly interesting, but we clearly don't understand it very well. You cannot explain the differences between a polyethylene and PVC, due to chain-branching or chain-configuration. Experiments have been done reducing PVC with lithium aluminum hydride to essentially a polymethylene-type polymer, a polyethylene model. When this experiment is done, the polymer molecule undergoes two major changes in its behavior. The first change is the melt viscosity is reduced and secondly, the melt elasticity of polymers is reduced. One can conclude from this type of experimentation, that the molecular architecture of the polymer is not responsible for the higher viscosity and elasticity of the PVC molecule. There are two possible rationalizations of melt viscosity behavior of PVC. The first explanation might be that we are dealing with a polymer, that contains a chlorine group acting as a large bulky side chain increasing the rigidity of the polymer chain which in turn increases the viscosity. The second potential argument is that PVC due to its polarity is highly associated in the solid state. It would be expected that such a material would have a higher viscosity behaving like a higher molecular weight polymer. This latter explanation is given some credence when one looks at the behavior in dilute solution. It is well known that PVC in dilute solution behaves as an associated polymer. Indeed, it is difficult or almost impossible to get a total disassociated PVC solution.

A second unique molecular property of PVC is the molecular weight distribution found in commercial resins. PVC is unique in the sense that it has a very narrow molecular weight distribution. Using weight to number average as a crude index of distribution, the values for PVC fall in the range from two to approximately four for all commercial PVC resins. In contrast, this ratio is anywhere from one to a hundred for the other common commercial polymers. We do understand the reason for this narrow molecular weight distribution of PVC as being due to the high chain transfer to the vinyl chloride monomer. This narrow range of molecular weight distribution also limits one in developing high shear rate processability of PVC without the use of additives.

In the polymer business we are always confronted with the problem of compromise between processability and ultimate properties of the processed polymer. In order to get easy processability, one tries to have as low molecular weight polymer as possible. On the other hand, to obtain desirable ultimate properties of the polymer, one would like to have as high a molecular weight as possible. In the case of PVC, the molecular weight is determined primarily by a polymerization temperature. There's little or no effect of the initiator concentration on the molecular weight of the polymer. As one increased the temperature of the polymerization, one decreases the molecular weight of the resulting polymer, although as we've said before, the molecular weight distribution is not changed. Unfortunately, the PVC has thrown us another ringer in its polymerization behavior. In order to get increased molecular weight, one lowers the temperature, but by just lowering the temperature, one also changes the conformation of the polymer chain. At lower temperatures, one increases the syndiotactic content of the polymer chain and this significantly affects the subsequent properties of the polymer. Commercial PVC normally produced in the range of 40-70°C has generally about 10-15% crystallinity, a molecular weight of ca. 100,000 and a syndiotactic ratio of about 54. Polymerizing PVC at lower temperatures, for example at 5°C, produces a polymer with a molecular weight of approximately 500,000 and the syndiotacticity changes from .54 to .57, a small change in the stereo-regularity. This moderately small change in the molecular weight and accompanying small change in syndiotacticity, causes a major change in the resulting polymer (28). Polymer produced at 5°C is virtually an intractable material and cannot be processed. Research is necessary in order to change the molecular weight and molecular distribution by other means rather than the temperature. By tricks in the polymerization methodology, PVC producers are attempting to produce PVC's with a higher molecular weight, and a broader weight distribution, and at the same time, with a decrease in syndiotacticity. It is hoped by this methodology one can produce a PVC which has better ultimate properties, and at the same time without a large sacrifice in processing properties.

It is not possible to talk about the processing of PVC without also discussing the uniqueness of PVC in respect to its thermal stability. It is impossible to process rigid PVC without the addition of thermal stabilizers. There are many potential causes of the thermal instability of PVC, but few people would agree as to the major causes (30). The widely accepted possible causes of instability are: 1) allylic chlorine structure, 2) unsaturation in the polymer, 3) long-chain branching, 4) hydroperoxide linkages, 5) carbonyl groups, 6) head-to-head configuration for the polymer. It is not my desire to review the literature on the thermal stability, just to touch upon some of the aspects which can affect the processability of PVC. To date, even with a large number of research papers appearing on the thermal stability of PVC, no conclusive unambiguous data has appeared, which would substantiate one or a combination of several of the above polymer defects which could explain PVC instability. Data which has been obtained on model compounds, suggest that the stability of PVC like materials should be far greater than those achieved by commercially available polymers. There is indeed some question as to what the ultimate stability of polyvinyl chloride could be in the absence of the afore mentioned defects. One thing is clear, the poor thermal stability of PVC limits the temperatures of PVC processing and this, of course, limits the lower limit of viscosity. It is unfortunate that the stability of PVC decreases with increase in temperature at a much faster rate than melt viscosity decreases with increasing temperature (29). It is this basic property of PVC that has intuitively led engineers in the past to develop compound additives which would allow one to process rigid PVC at lower temperatures with better controlled thermal conditions.

The decade of 80's, will be studying ways to better process PVC. These studies are just as challenging or more challenging than those areas of research studied during the 60's and 70's. Understanding of the role of the resin particulate nature, particularly in regard to the role of the outer skin, on the processing and additive interaction properties of PVC will have to be developed. The understanding of the fusion process and processing characteristics of a resin lies in the understanding and developing of a better knowledge of exactly what the nature of the flow unit is. This seems like a trivial question, but indeed has many ramifications. Evidence in the literature has already been established that PVC does not flow by a molecular process, but indeed the mechanism is more described as being particulate. It has also been established that previous work history or processing history, strongly affects the rheological behavior of PVC. In other words, the target and the material is changing constantly with the history of the sample. The role the crystallites play in the processing and the ultimate properties of the plastic is also an area in which needs extensive and definitive research. A third area of major lack of understanding of PVC is the development of physical properties by the processed compound. It is been shown a decade or more ago that PVC without losing its particulate structure, can exhibit tensile properties, equivalent to those materials that have been completely processed and have had all of their particulate structure destroyed. The understanding of the interdiffusion boundary between the particles, whether we are talking about a hundred micron, or one micron or the hundred Å° particle, should be better understood in order to

obtain the maximum utilization of PVC. This latter subject leads us into the study of the mechanics of the polymer and the fracture properties of compounds that we are now using. It also leads us to the understanding and study of so-called alloy systems, polymer-polymer compatible systems, using PVC as the base material to develop better, stronger and more readily processible materials in the future. The property which has been studied extensively, but still eludes PVC scientists is the underlying causes for thermal instability. Identification of these principles and correction of the polymer defects causing instability will lead to a major breakthrough in processing approaching the ideal of a no additive PVC extrusion.

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