

Effects of Dry Blending on Morphology of PVC Powder Particles

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Synopsis

Mass and suspension PVC were blended on a Fielder mixer and changes in powder morphology and additive distribution investigated. The techniques used to characterize and assess processing behavior have included microscopy, density, size analysis, torque, and capillary rheometry. The particulate structure of PVC remained intact, and there were no pronounced differences in the processability of blends discharged at different temperatures. In the absence of shear PVC particles are largely unchanged in character. Solid additives do not appear to enter into resin particles while liquid stabilizer readily does so.

INTRODUCTION

A number of workers¹⁻⁴ have examined the dry blending behavior of commercial PVC formulations and the effects of groups of additives on blending and subsequent processing behavior. This paper is concerned with changes in the morphology of PVC powder particles as a result of dry blending. If there is a gross modification of the PVC morphology as a consequence of blending, then it might be expected that subsequent processing could yield products of varied properties.

More simple systems have been chosen in order to examine fully specific aspects of blending. These were:

- (1) An assessment of the degree to which PVC powders themselves are affected by the blending cycle: specifically, changes in the density, size distribution, and internal and surface structure of particles arising from blending.
- (2) The behavior of additives during the blending operations and their disposition in the dry blend. Their location may give a better understanding of the role they play during processing.
- (3) The establishing of an optimum blending cycle in terms of temperatures, times, and mixing speeds, which would give a consistent and satisfactory product with minimal batch-to-batch variations.
- (4) The processability of blends discharged at different temperatures from the mixer.

EXPERIMENTAL

Formulations

Two commercial grade PVC resins were used, namely: Breon M80/50 Mass PVC (BP Chemicals, Ltd.) and Corvic D55/09 Suspension PVC (ICI, Ltd.). The additives, solid tribasic lead sulphate stabilizer (TBLS), liquid thiotin stabilizer

TABLE I
Lead Formulation (A)

PVC resin	100 phr by weight
TBLS	4 phr by weight
Calcium stearate	1.5 phr by weight

(Stanclere T135), and calcium stearate lubricant were supplied by Akzo Chemie UK, Ltd. They have been added at levels normally used in commercial productions.

The formulations employed are shown in Tables I and II.

Preparation of Blends

Blending was carried out in an 8-L T. K. Fielder dry blender fitted with stock temperature measurement facilities, jacket temperature control, and a separate cooling chamber or cooler unit. Blending conditions are set out in Table III.

Apart from optimizing the blending cycle, it was also intended to find a set of operating variables which gave rise to blends which were spatially homogeneous and whose powder particles were significantly modified in shape, size, and topographical features.

In the lead formulation either or all the additives were added at the start of the blending operation. Variations included adding the lubricant at 20°C before the final discharge temperature. The tin formulation required steam heating of the mixer as insufficient frictional heat would be generated to raise the temperature of the mix over 100°C. For this formulation lubricant was added at the start of blending.

Microscopy

Light, conventional transmission and scanning electron microscopy have been used to study microstructure. In general the use of sectioning techniques to study the internal structure of powder particles was chosen as more direct and unambiguous information is usually available by these methods.

A few powder particles were embedded in an Araldite epoxy resin, contained in a gelatin capsule.⁵ These were then sectioned, either using a Leitz base sledge microtome or an LKB ultratome, according to the section thickness required.

For scanning electron microscopy work the powders were stub-mounted in the usual way and sputter-coated with gold after precoating with carbon. The light microscopy techniques employed were mainly phase contrast and differential interference contrast.

TABLE II
Tin Formulation (B)

PVC resin	100 phr by weight
Stanclere T135	3 phr by weight
Calcium stearate	0.5 phr by weight

TABLE III
Blending Conditions

	(A) Lead blend	(B) Tin blend
Weight of charge (kg of PVC)	3	2
Rotor speed (rpm)	4000	3500
Jacket temperature (°C)	—	70
Temperature at stabilizer addition (°C)	—	50
Cooler unit rotor speed (rpm)	1000	1000
Cooling period (min)	2-3	2-3

Density

Apparent density was determined by the British Standard Institution Method BS 2782, Part 5, Method 501A, 1970, which involved measuring the volume of a known weight of PVC powder in a 100 cm³ standard laboratory measuring cylinder. The powder was allowed to settle under gravity, without any external packing influence. For bulk density, 100 g of powder was vibrated to a constant volume in a cylinder fitted into a tap-pack volumeter.

Particle Size Analysis

Two standard techniques were used for the size measurements. Photomicrographs of the particles were analyzed using a Zeiss TGZ3 semi-automatic particle size analyzer. The parameter recorded was chosen to be the equivalent projected area of the powder particles, although other modes are available and are currently under investigation. As a much quicker alternative, the standard sieve method was also used. Mesh sizes were 45, 53, 75, 106, 125, 150, and 180 μm , the sample size was 50 g, and the vibration time was 15 min.

Assessment of Processability of Blends

Two methods were used to assess the ease of processing blends discharged at different temperatures from the mixer.

Capillary Rheometry

A Davenport capillary rheometer with barrel temperature of 180°C was used. The capillary die was 20 mm long with a diameter of 2 mm. The powder blends were charged into the rheometer, compressed, and held for 5 min before being extruded at a variety of shear rates, noting the extrusion pressure. Three measurements were made on each blend to ensure reliability of data and the average taken. No corrections were applied to the results since only a comparison of relative flow properties was needed.

Torque Rheometry

The test conditions on the Brabender plastograph are shown in Table IV.

TABLE IV
Test Conditions on Brabender Plastograph

Temperature of mixing chamber (°C)	140
Sample charge (g)	30
Rotor speed (rpm)	20
Load on ram (kg)	4

RESULTS AND DISCUSSION

The effect of mixer discharge temperature on apparent density is shown in Figure 1. For both mass and suspension PVC, a higher discharge temperature results in blends of increased density. Mass PVC blends were observed to have higher density values than those of suspension PVC.

Figure 2 shows that mass PVC has a narrower particle size distribution than the suspension PVC. Figure 3, which are micrographs of the PVC particles viewed by reflected light, illustrates that mass PVC has greater regularity in shape. If some DOP is added to the particles and viewed by transmitted light under the microscope, the mass PVC particles are observed to lighten more evenly as they absorb the DOP. The suspension particles absorb the DOP much more slowly overall, and have a greater variation of light and dark portions (see Fig. 4).

A broad particle size distribution would be expected to result in a better packing and hence higher density as smaller particles could fill the spaces in between large ones. The finer particles may, however, be more loosely packed as arches and bridges are formed, thus nullifying the effect of particle size variation. A closely packed more uniform particles would then have less voidage and hence higher density. It is therefore not any broadening of distribution that will result in an increase in density. Generally, as the distribution is broadened over a narrow range, packing efficiency falls and, consequently, the density. Heywood⁶ puts the optimal density that can be achieved by having the right type of size distribution as being a bimodal distribution of approximately 6:1 size ratio.

The higher density values of mass PVC can therefore be attributed to its narrower particle size distribution, greater regularity in shape, and more uniform porosity.

Morohashi⁷ has suggested that the increase in bulk density with mixer discharge temperature is due to particle size reduction. It will be shown later that, even with the Zeiss TGZ3, which gives a more critical and interpretable assessment of size distribution, no significant change in size distribution was found in blends discharged at different temperatures.

Boulton⁸ considers the main factor to be a more effective packing resulting from deagglomeration or the collapse of voids between particles during blending. Also, the additive in the blend may so affect the surfaces of the polymer particles as to alter the packing characteristics and thus the bulk density. Both suggestions appear to be supported by microscopy. For instance, Figures 5 and 6, which are scanning electron micrographs of blended and unblended PVC particles, reveal that there is a slight rounding of the profile of the particle. The spongelike

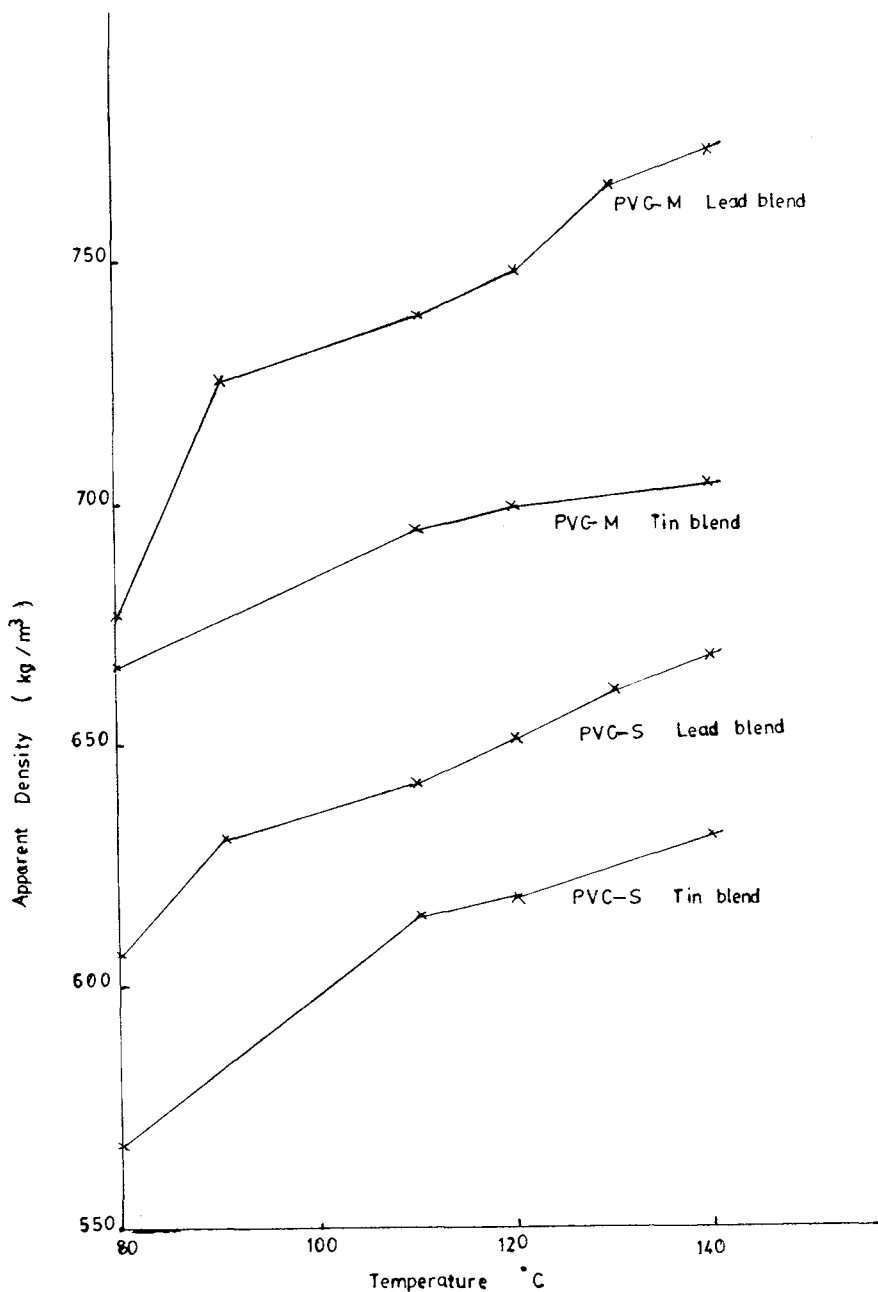


Fig. 1. Change in apparent density with mixer discharge temperature.

agglomerated microgranules clearly seen in Figure 6(a) are not so evident in Figure 6(b), where they appear to have been flattened out or fused together and covered by a "paste." In Figures 9 and 10, where the polymer was blended with liquid additives, the microgranules are clearly observed. This "paste" will be shown later to be the solid additives on the powder surface (see Fig. 14). It seems

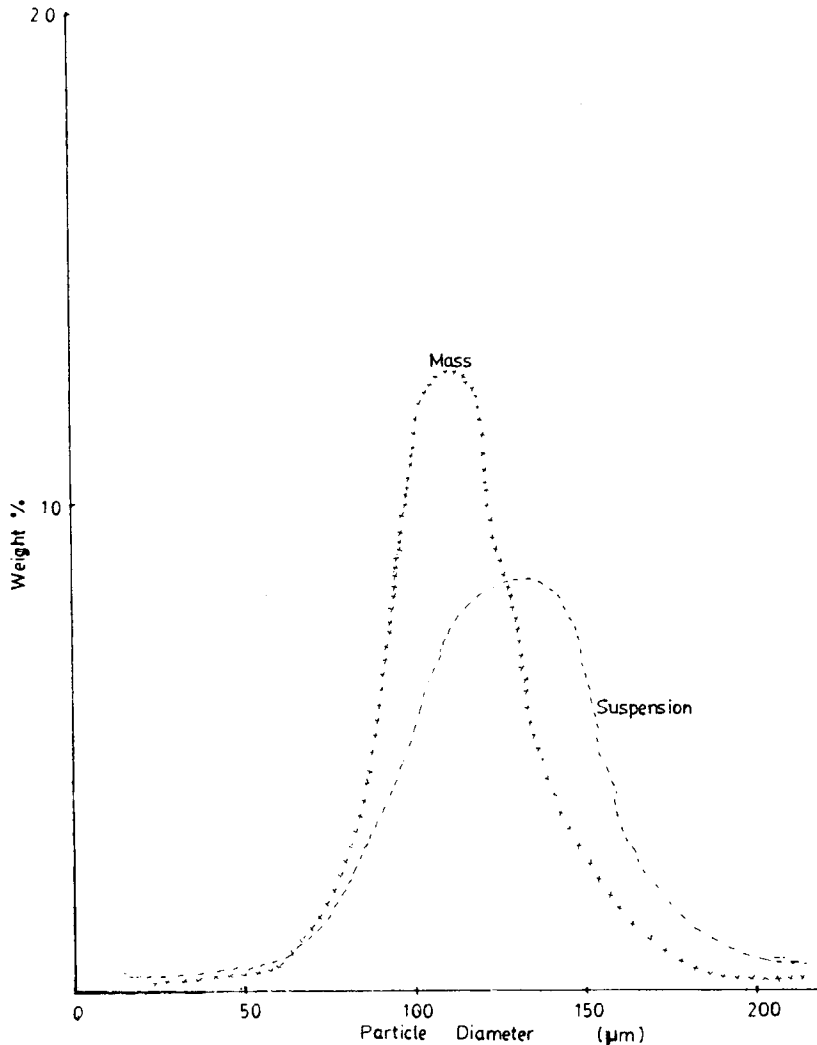


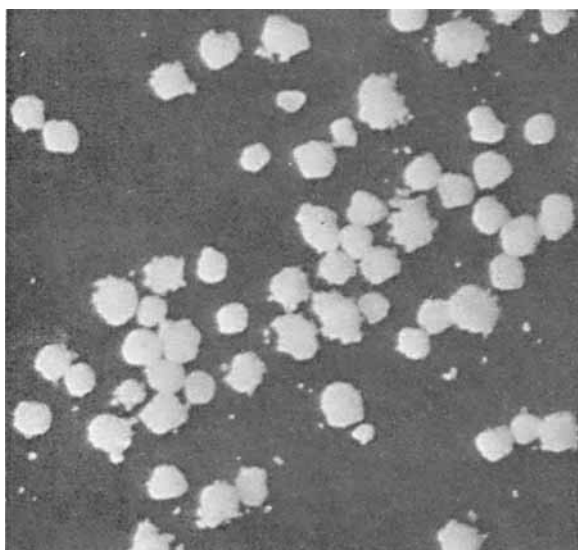
Figure 2. Particle size distribution of mass and suspension PVC.

therefore that the forces experienced by the particles during the dry blending operation and the infill of additives result in the rounding and smoothing of the surface and thus affect the bulk density.

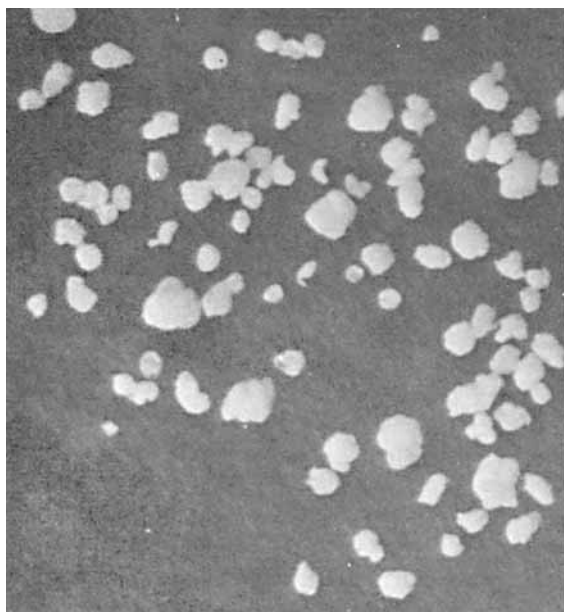
Effect of Blending on Particle Shape and Structure

Figures 5 and 6 also show that there is no marked change in particle shape after blending, although a gradual smoothing of the particle surface is observed. With nodular particles of PVC it has proved difficult to establish a shape parameter of satisfactory sensitivity. Thus one is forced to rely heavily on a subjective assessment of the degree to which the particles become rounded after dry blending.

A characteristic of suspension PVC unlike mass PVC is that the surface is



(a)

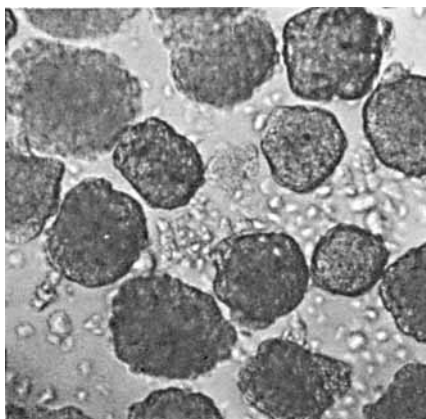


(b)

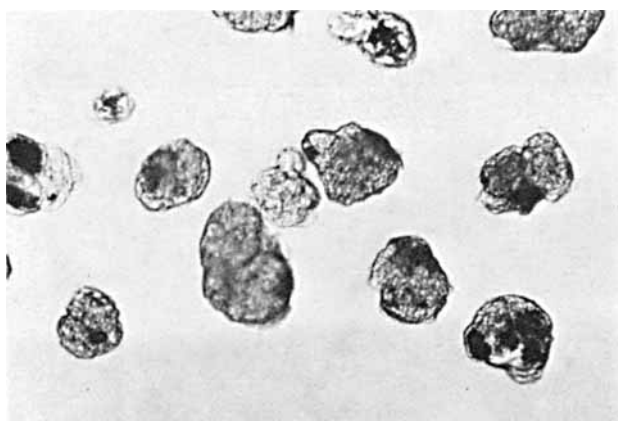
Fig. 3. Optical micrographs of PVC particles viewed by reflected light: (a) mass PVC; (b) suspension PVC. Magnification: $\times 60$.

covered by a "skin" or "membrane." However, the extent of this "skin" is known to vary within very wide limits. Thus in Figure 5(a) the presence of a "skin" over much of the surface is apparent compared to Figure 6(a).

It is not unreasonable to expect the blending operation to lead to gross damage or rupture of the skin, which would allow additives to penetrate into the polymer more easily. Rougher surfaces would also lead to greater generation of frictional



(a)



(b)

Fig. 4. Optical micrographs of PVC particles in DOP viewed by transmitted light at 80°C: (a) mass PVC; (b) suspension PVC. Magnification: $\times 60$.

heat and, consequently, shorter blending cycles. No such general rupture of the “skin” as a result of the blending operation was observed.

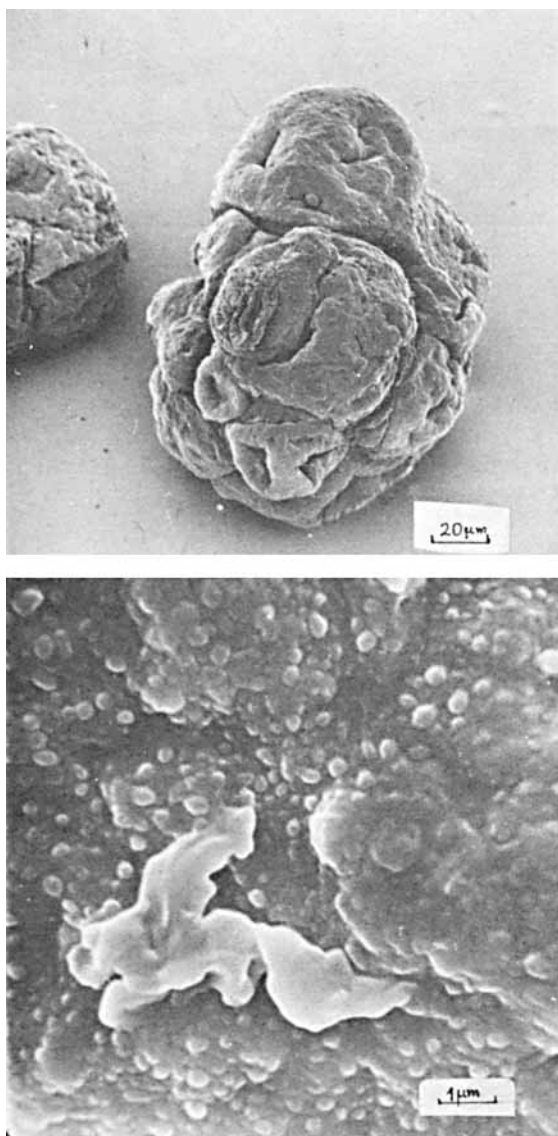
A close look at Figure 8, which are optical micrographs (phase contrast) of thin sections of suspension PVC particles before and after blending, reveals a peripheral layer is present. This is further amplified by referring to Figure 5 again.

Because of this apparent resistance of PVC particles to breakup or gross deformation during blending, the resin was subjected to a more severe impact treatment at temperatures above and below ambient, using a jet mill. Although there appeared to be some rounding or smoothing of the particle surfaces, there was no evidence of particle disintegration or of severe deformation.

Further attempts were made to deform the polymer particles by thermal treatment alone. Individual particles were subjected to various temperatures for a range of times. Their shape and surface texture were examined both before and after the treatment. Again the material showed remarkable resistance to gross modification of shape and surface texture. This is illustrated by Figure 7, which shows suspension-polymerized particles after 5 min and 10 min at 200°C.

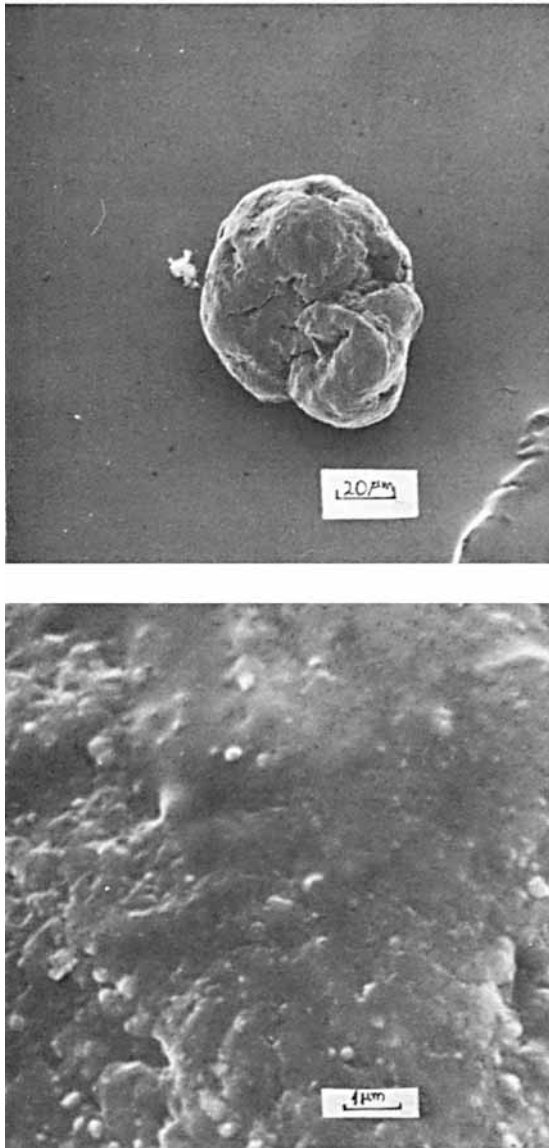
Only in the latter case is there complete smoothing of the surface. Where the polymer has been blended with stabilizer and lubricants, the smoothing effect appears to be even more delayed.

Typical phase contrast micrographs of thin sections of blended and unblended PVC particles are shown in Figure 8. The internal particle structure is observed in all cases, and it is not affected by blending. Electron microscopy confirmed that the particulate structure of PVC remains intact even in specimens subjected to extended blending cycles in the Fielder blender. Thus in Figures 9 and 10 the microgranules are observed as in unblended polymer particles in Figures 5(a)



(a)

Fig. 5. Scanning electron micrographs of the surface of a suspension polymerized PVC particle: (a) unblended; (b) lead blend discharged at 120°C.



(b)

Fig. 5 (Continued from the previous page.)

and 6(a). It is suggested that the “paste” of solid additives on particle surface prevents similar observation in Figures 5(b) and 6(b). Comparing Figures 11(a) and 11(b) the primary particles, i.e., the 1–2- μm particles, are still evident. It must be concluded that despite the open structure of PVC particles very little particle modification is to be expected in the normal blending process.

Effect of Blending on Particle Size Distribution

At the outset of this investigation into the effect of blending cycle on the particle size distribution, it was thought prudent to compare closely size distribution results by two methods.

Using the methods described above such a comparison requires a recalculation of one set of results so that the data are comparable in terms of the parameter being measured. To do this, the assumptions were made that individual particles are roughly equidimensional and that large and small particles have similar density. Microscopy suggests both these assumptions are valid. Thus an examination of the mass PVC on a stereomicroscope revealed a substantial absence of "glassy" particles, i.e., particles of low porosity.

Figure 12 shows the size distribution of unblended suspension PVC by the two methods. The two sets of results show real differences. They can be interpreted by postulating that particles in the interval 150–180 μm are mainly agglomerates,

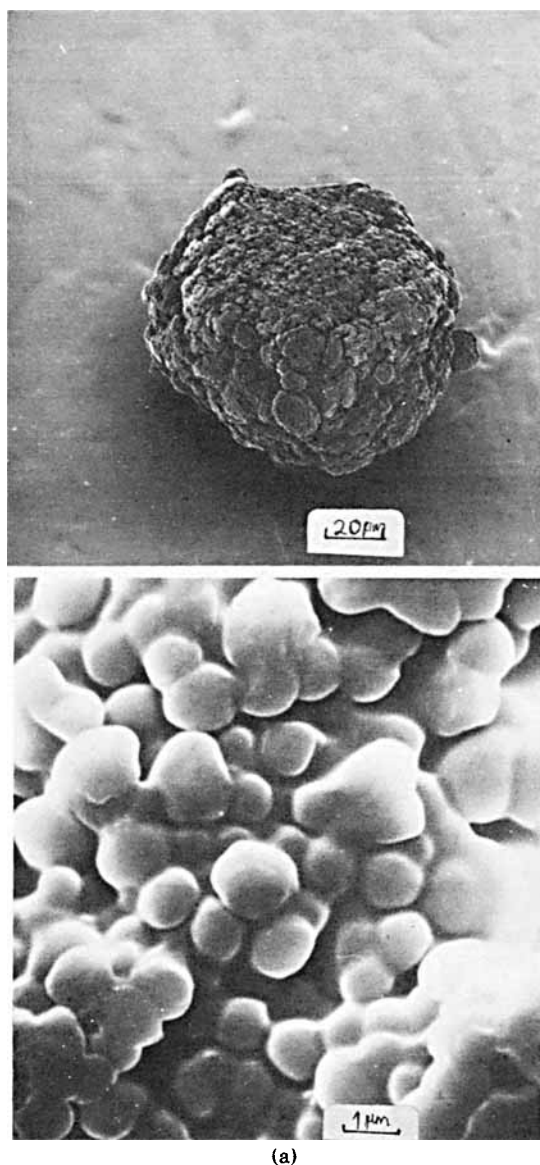
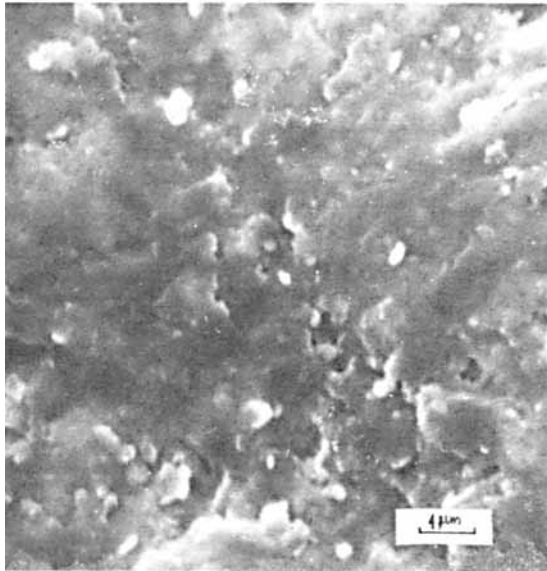
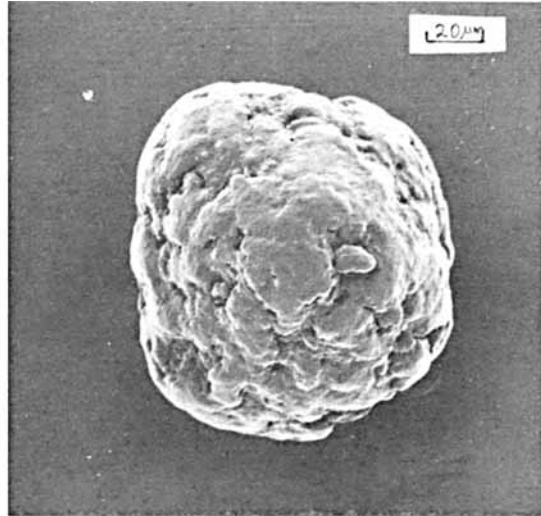
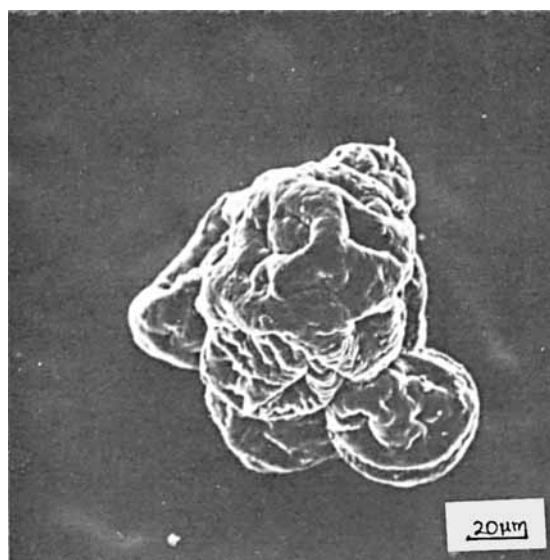


Fig. 6. Scanning electron micrographs of the surface of mass polymerized PVC particle: (a) unblended; (b) lead blend discharged at 120°C.

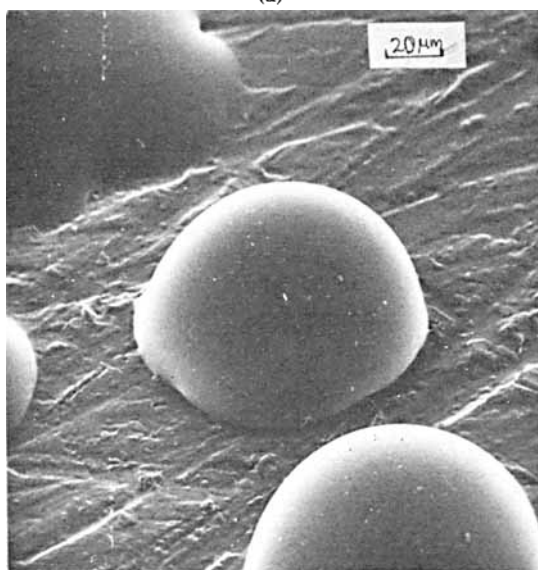


(b)

Fig. 6 (Continued from the previous page.)



(a)

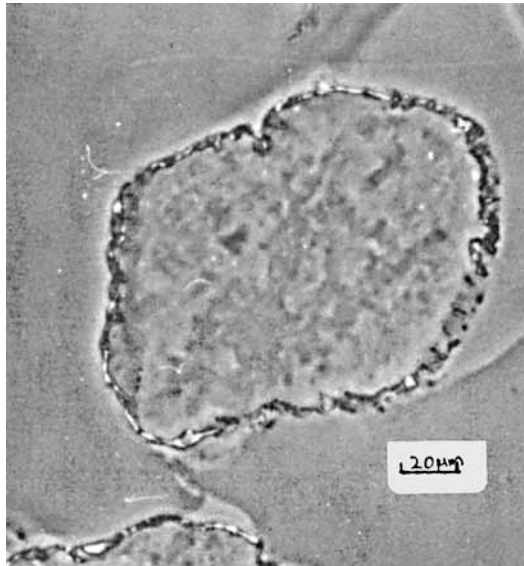


(b)

Fig. 7. Effect of heat on particle topology: (a) 5 min at 200°C; (b) 10 min at 200°C.



(a)



(b)

Fig. 8. Optical micrographs (phase contrast) of microtomed sections of suspension-polymerized PVC particles: (a) unblended; (b) lead blend discharged at 120°C.

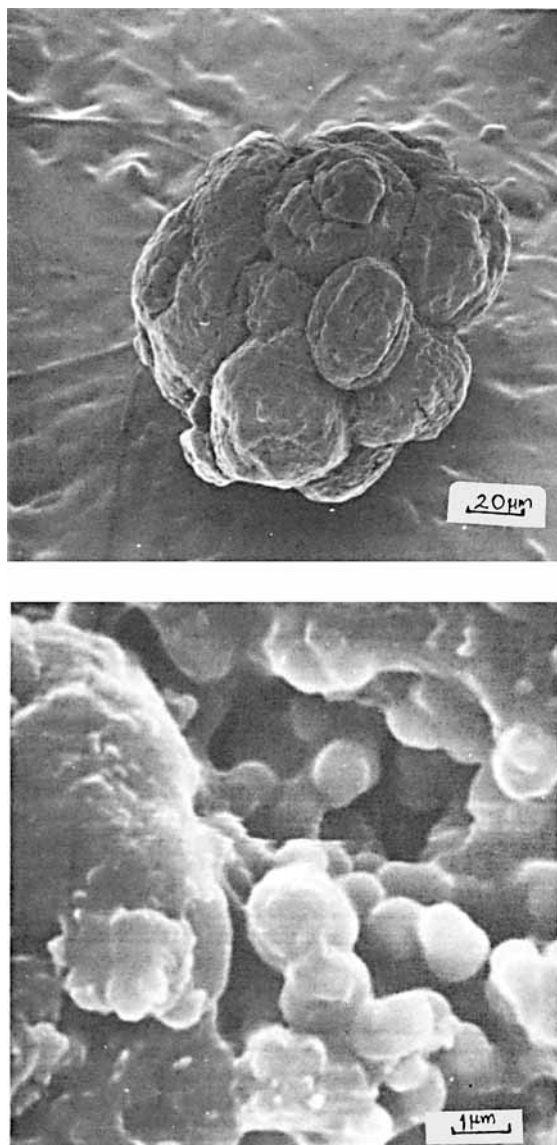


Fig. 9. Scanning electron micrographs of the surface of a suspension-polymerized PVC particle (tin blend) discharged at 120°C.

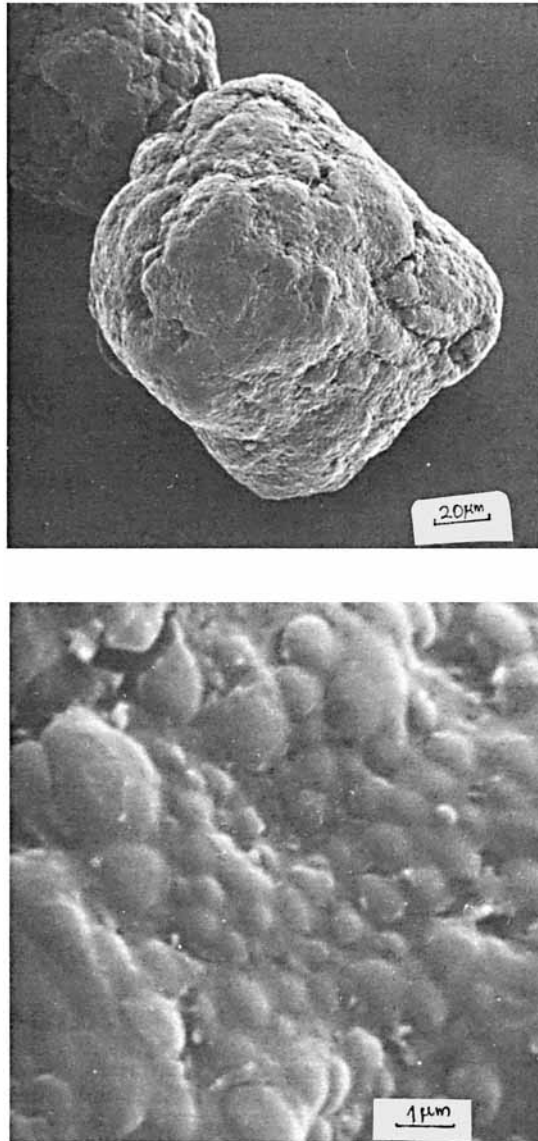
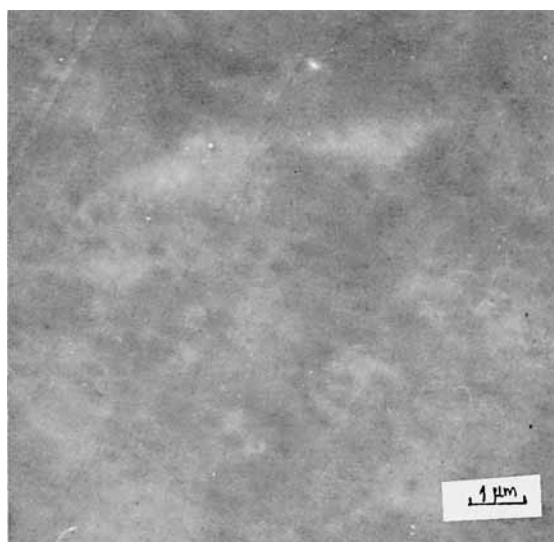


Fig. 10. Scanning electron micrographs of the surface of a mass-polymerized PVC particle (tin blend) discharged at 120°C.



(a)



(b)

Fig. 11. Transmission electron micrographs of a PVC particle showing the persistence of particulate structure after blending: (a) unblended; (b) blend.

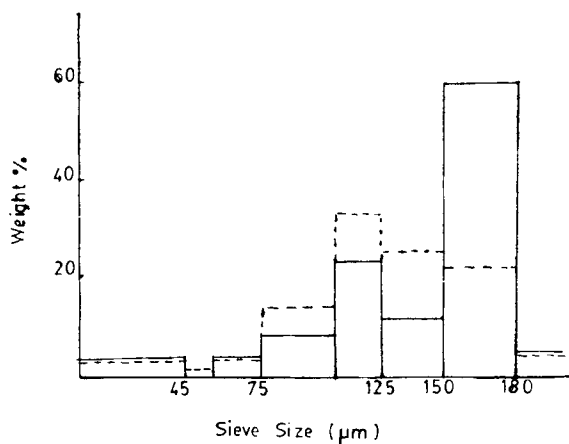


Fig. 12. A comparison of size assessment methods. (—) Sieves; (---) Zeiss Counter.

which are distinguished as such by the subjective sizing counter method but not by the sieve analysis. The counter method distributes many of these larger "particles" over the smaller class intervals, roughly in proportion to those passing through the 150- μ m mesh. It is reasonable therefore to conclude that a critical analysis of powder particle size distribution is better carried out using the Zeiss counter as it allows subjective discrimination of agglomerates.

The main drawback is that using the Zeiss counter is relatively tedious as it requires a very large number of particles to be measured in order to obtain a reproducible and accurate result. If, for convenience, sieve analysis is used, then it is necessary to exercise caution in interpreting differences in distributions in the upper size ranges.

Figure 13 shows typical size distribution of blends discharged at various temperatures as determined by the Zeiss counter. No substantial changes are observed. Indeed any changes could be accounted for by the breakup of loosely bound agglomerates of small or large diameter powder particles. It seems this is achieved quite early in the blending operation.

Additive Distribution and Dispersion

Thin sections of individual powder particles examined in light and electron microscopes show that the solid additives are usually well distributed and located on the powder surface. Only the very shortest blending cycles or the least intensive ones fail to achieve this kind of distribution.

Figure 14 is a transmission electron micrograph of a thin section of suspension PVC lead blend. There is little penetration of the powder particle. However, where small additive particles such as TBLS are involved, one would expect they are able to enter the pores and convolutions of the powder particle surface. This effect should, from the powder particle morphology, be particularly noticeable in the case of mass polymer, as Figure 15 illustrates.

The behavior of the liquid stabilizer during the blending operation is more complex. It is readily absorbed into the PVC particles, but its distribution is

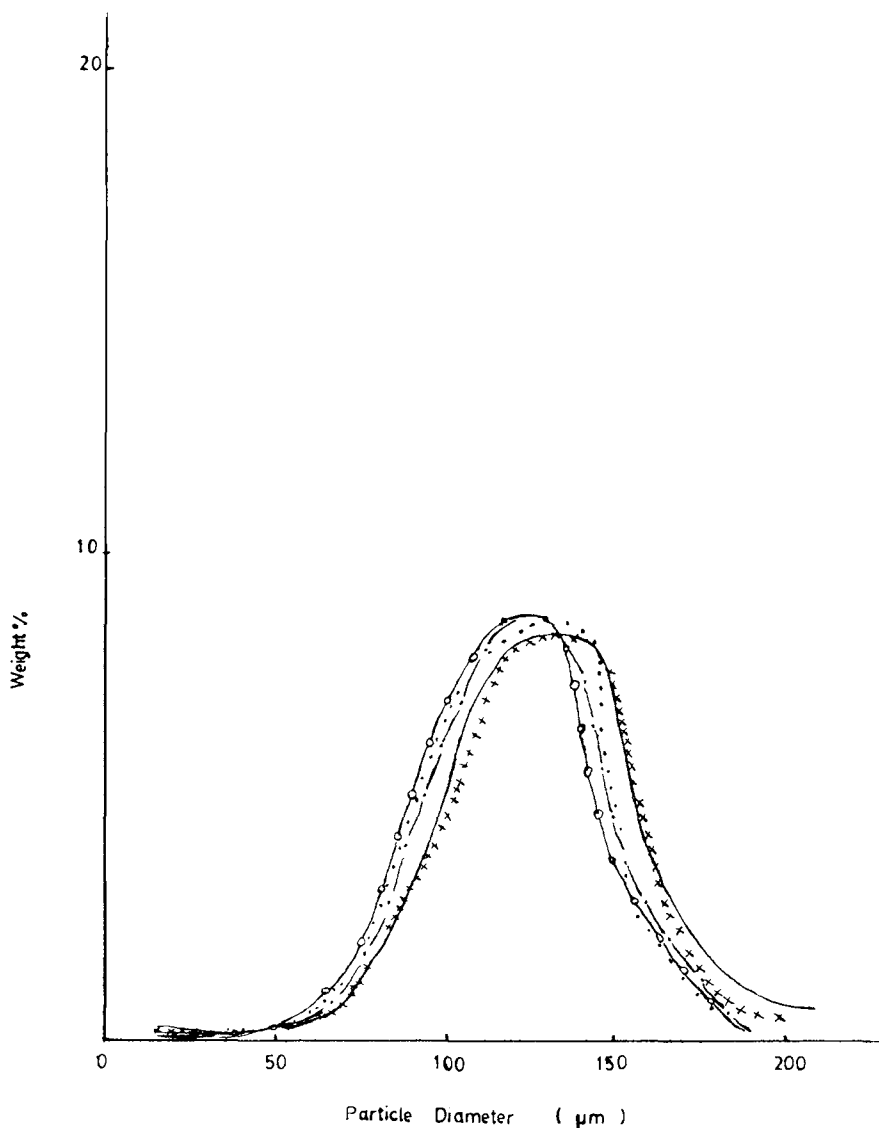


Fig. 13. Particle size distribution of suspension-polymerized PVC blends discharged at various temperatures (lead formulation). (—) PVC-S; blends at (×) 80°C, (· · ·) 110°C, (— · —) 120°C, (—○—) 140°C.

not uniform. DTA measurements show that this stabilizer lowers the T_g of the polymer thus exercising a plasticising effect. The magnitude of these effects can be correlated with blending conditions as they become more pronounced at higher blend discharge temperatures. At these temperatures the liquid stabilizer has fully dispersed into the resin—into the microgranules and the interstices between them. Certainly this would impart better heat resistance to the formulation.

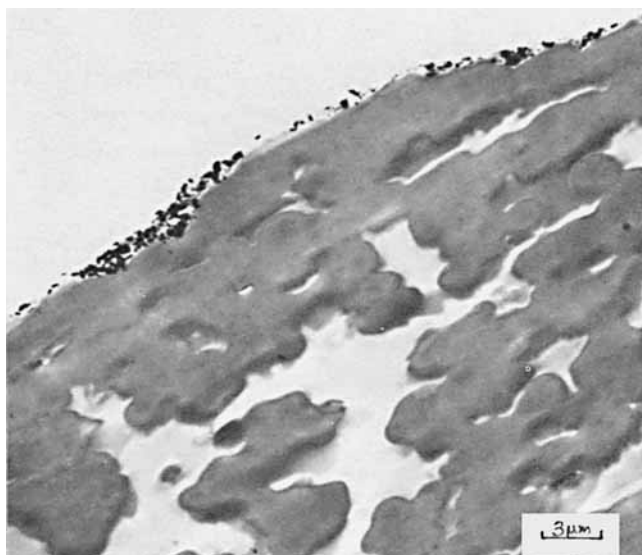


Fig. 14. Transmission electron micrograph of ultramicrotomed section of PVC powder blend showing additives on surface of a powder particle.

Effect on Processing Behavior

Figures 16 and 17 show extrusion pressure as a function of shear rate. No substantial difference is observed for any given formulation. However, the difference in the effect of the two additives is clearly evident. Thus the extrusion pressure for the tin blends is much lower than for the lead blends. Acting as a plasticizer, the tin compound lowers the viscosity of the polymer and eases processing. Results obtained from the Brabender Plastograph reveal no marked

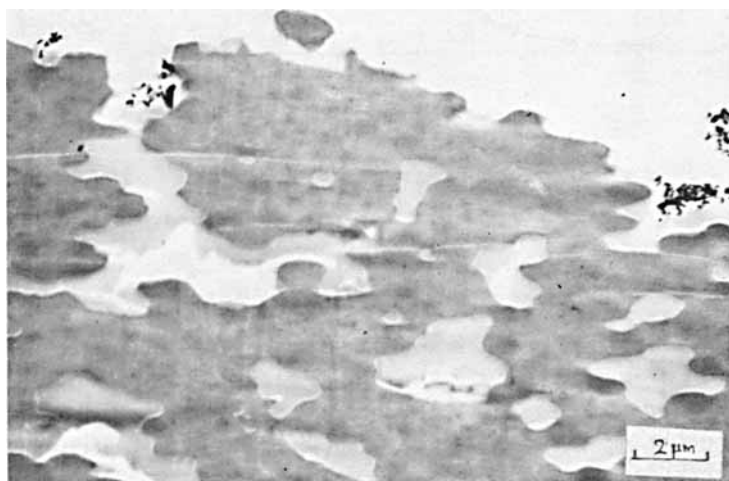


Fig. 15. Transmission electron micrograph of ultramicrotomed section of mass-polymerized PVC particle (blended).

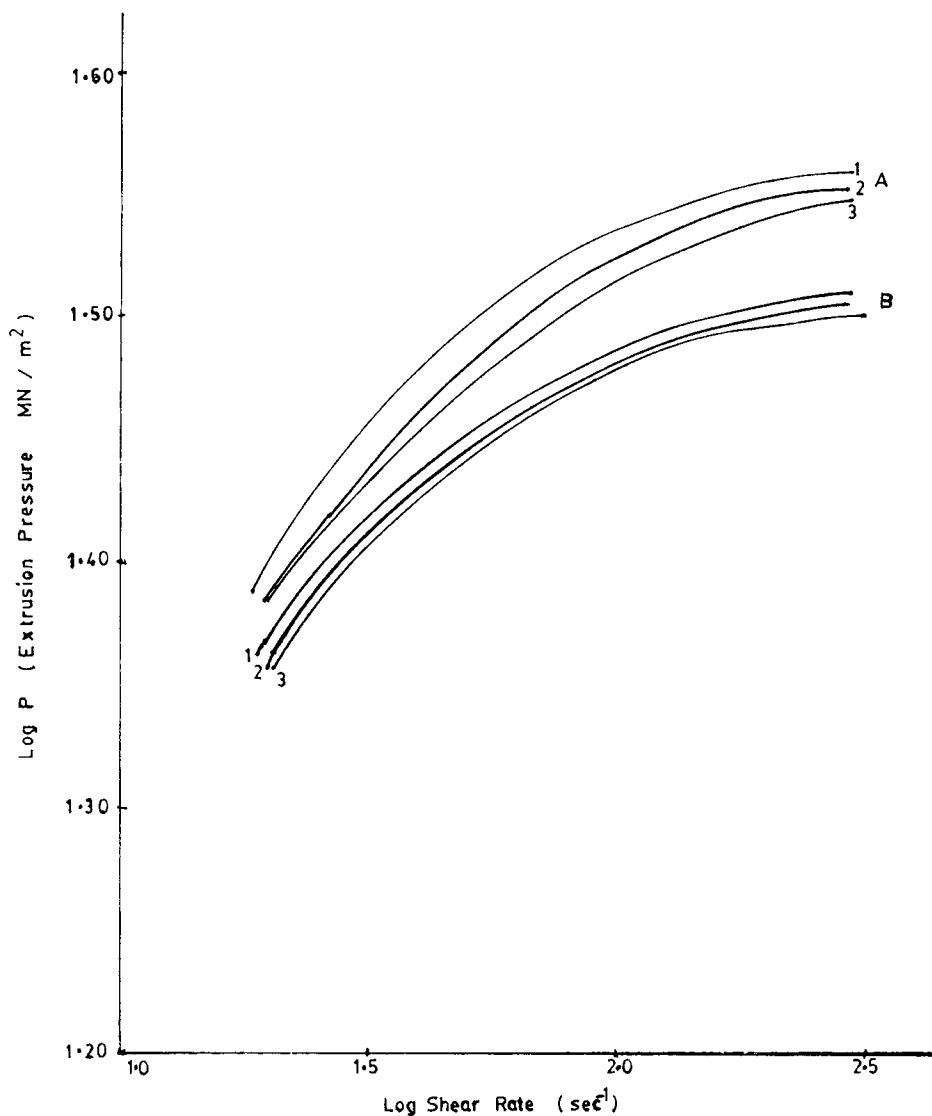


Fig. 16. Flow curves of suspension polymerized PVC blends discharged at various temperatures ($^{\circ}\text{C}$): (1) 120; (2) 110; (3) 80; (A) lead formulation; (B) tin formulation.

differences in the fusion characteristics of material discharged from the blender at different temperatures. Since the morphology of PVC is largely unchanged by the Fielder blending operation, the fusion characteristics or ease of processing of the blends for a given formulation should be expected to be similar. In fact, Faulkner⁹ has compared the temperature-torque curves of a dry blend, partially fused granules, and reground extrudate of the same PVC compound. He found that, in the first two in which the particulate structure of PVC was essentially preserved, the curves were similar. But the reground extrudate had a different curve.

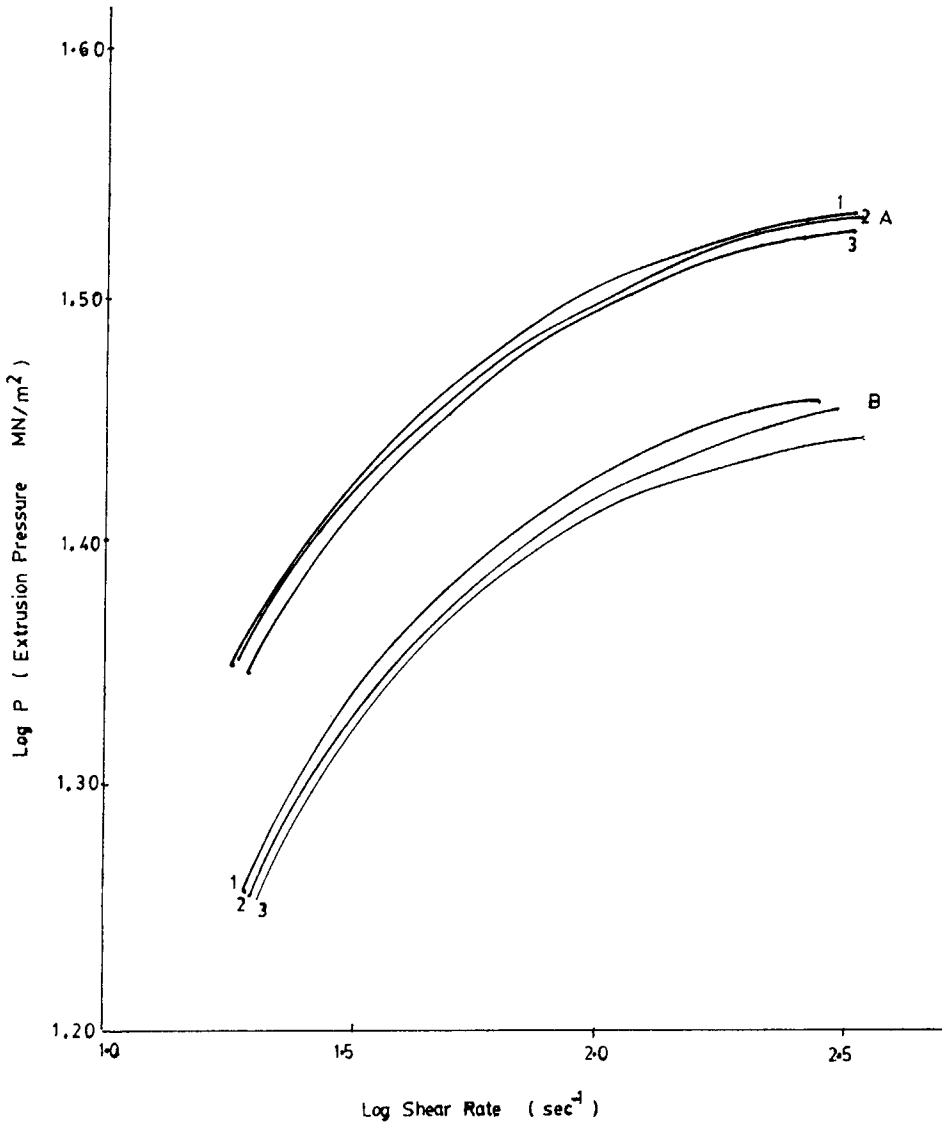


Fig. 17. Flow curves of mass polymerized PVC blends discharged at various temperatures ($^{\circ}\text{C}$): (1) 120; (2) 110; (3) 80; (A) lead formulation; (B) tin formulation.

CONCLUSIONS

The general conclusion from this work using the T.K. Fielder mixer is that the main effect of blending PVC compound is a spatial rearrangement of the ingredients, with only minor modifications to particle shape, size, and surface texture. Indeed, attempts made to exaggerate grossly the severity of treatment have failed to significantly increase these small modifications, suggesting that, even with much higher peripheral rotor speeds, little modification is to be expected. In practice, peripheral rotor speeds are independent of the size of the machine.

The repartition of additives, the breakdown of agglomerates existing in the starting materials, and the densification of the PVC powder seem to be achieved early in the blending as size analysis of blends discharged at various temperatures are not significantly different and the biggest increase in density occurs between the start and mix temperature of 80–90°C.

As a result of the PVC morphology being largely unchanged by blending, the ease of processing is not appreciably affected by blend discharge temperature. It is highly probable that only by shearing the PVC powder can changes be made to particle structure which would noticeably affect the subsequent handling and processing characteristics of the material.

Solid additives such as TBLS with high melting points are not absorbed into PVC particles but coat the surface. Liquid tin stabilizer, on the other hand, diffuses into the resin particle in a way similar to plasticizers. Blending to high temperatures will ensure the liquid stabilizer has fully diffused into the resin.

References

1. G. M. Gale, Rapra Research Report, 172.
2. D. R. Jones and J. C. Hawkes, *Trans. Plast. Inst.*, 773, (Dec. 1967).
3. C. Guimon, Society of Plastics Engineers Annual Technical Conference, Detroit, May 1967, Vol. XIII.
4. Y. Shinagawa, *Plast. Ind. News, Jpn.*, 65, (May 1973).
5. A. M. Glauert and R. H. Glauert, *J. Biophys. Biochem. Cytol.*, 4, 191 (1958).
6. H. Heywood, *Powder Metall.*, 7, 1 (1961).
7. H. Morohashi, *Jpn. Plast.*, 2, 27 (1968).
8. A. J. Boulton, in *Developments in PVC Production and Processing*, Applied Science, London, 1973.
9. P. G. Faulkner, *J. Macromol. Sci. Phys.*, B11, 251 (1975).

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