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COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES

WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

SUB-PRIMARY PARTICLES IN PVC— IDENTIFICATION AND ELUCIDATION OF THEIR ROLE DURING FLOW

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SUB-PRIMARY PARTICLES IN PVC: IDENTIFICATION AND ELUCIDATION OF THEIR ROLE DURING FLOW

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A wide range of morphological and rheological techniques, contributed by nine laboratories, are used to identify the sub-primary structure of PVC and elucidate its role during flow. It is concluded that the most likely flow unit in unplasticised PVC is an approximately spherical domain of about 100nm diameter which is not of itself deformable. The internal structure of such domains is formed of smaller structures on the 10nm scale held together internally by 'crystallinity' acting as cross-links. The connective tissue between the domains appears to be very highly deformable, and low molecular weight polymer may lubricate the relative movement between the flow units.

INTRODUCTION

PVC is commonly processed below its final melting point and the flow processes are usually assumed to be particulate rather than molecular. Many different size particles have been identified and Geil(1) has recently proposed a standardised description as follows:

Approximate size in typical PVC	Origin or description
100 µm	Free flowing at room temperature
10 µm	Formed during polymerisation merging of 1µm particles
1 µm	Formed from single polymerisation site at conversions of 10-50%. Commonly called "primary" particles
100 nm	Presence not clearly proven, possibly formed by mechanical working within or from 1µm particles
10 nm	Crystallite or nodule?

The nature, and indeed the existence, of the sub-primary particles is still a subject of debate. The most detailed studies of such particles have been in plasticised compounds(2) leaving open the speculation that the structures are the result of plasticisation rather than natural to the PVC. The objective of this collaborative study of the IUPAC Working Party on the "Structure and Properties of Commercial Polymers" was 'to identify and understand the nature of the sub-primary particles in PVC, if they exist as active structural units, to elucidate their role during flow, and to study how they are influenced by processing history'. An additional objective of the programme, which has not so far been carried through, was to study their influence on mechanical properties.

The active participants in this collaboration are identified in the text as follows:

BASF	BASF Aktiengesellschaft, Ludwigshafen, Germany
BP	BP Chemicals Ltd, Penarth, UK
BW	Borg-Warner Chemicals, Amsterdam, Netherlands
CW	Case Western University, Cleveland, USA
Huls	Chemische Werk Huls AG, Marl, Germany
ICI	ICI Ltd, Plastics Division, Welwyn Garden City, UK
M	Montecatini Edison SpA, Bollate, Italy
RP	Rhone Poulenc Industries, Antony, France
S	Solvay et Cie, Bruxelles, Belgium

MATERIALS USED IN THE STUDY

Working on the assumption that the sub-primary particle structure would be influenced by the polymerisation conditions the Working Party selected three commercial polymers of ISO K value 65 polymerised by emulsion, suspension and bulk technologies. All samples were compounded with standard, non-proprietary, formulations of stabiliser and lubricant at the same high temperature to eliminate the primary structure - details of the compounding histories are given in Appendix 1.

PRELIMINARY INVESTIGATION

There is no significant difference in the morphology of the suspension and bulk polymers compounded in either way. The emulsion polymer has a distinctly lower viscosity than the other resins, but also a substantial memory of the primary particle structure. The suspension and bulk polymer compounds made by twin screw extrusion using the tin stabilisers have a generally higher viscosity than corresponding compounds made on the Banbury using lead stabilisers (BW): this difference may be associated with the increased molecular weight of the former compounds (Appendix 2), or with differences in lubrication.

A description of the differences observed between the bulk and suspension and the emulsion polymer are appended (Appendix 3). Detailed study of the sub-primary structure was concentrated on the bulk polymerised sample Banbury compounded.

MOLECULAR STRUCTURE, MORPHOLOGY AND RHEOLOGY OF BULK AND SUSPENSION POLYMERS

Molecular Structure

Both bulk and suspension polymerised samples are of narrow molecular weight distribution ($\bar{M}_W/\bar{M}_N$ = 2) having weight average molecular weight about 75,000. The suspension polymer is of slightly higher molecular weight (Appendix 2) and in line with this observation all participants observed that it has a slightly higher viscosity. Apart from this slight difference in molecular weight no significant differences were detected between the two polymers. To limit the experimental programe the more detailed measurements were carried out only on the bulk polymer compounded by Banbury mixing.

The molecular structure may be utilised as a scale against which to compare the morphology as follows:

Weight average molecular weight	75,000
Weight average degree of polymerisation	1,200
Chain length ($\bar{M}_W$) fully extended	250 nm
Chain thickness	0.54 nm
Diameter of random coil ($\bar{M}_W$)	20 nm

Within the volume of one random coil ($\bar{M}_W$) there would be space for about 100 molecules ($\bar{M}_N$).

Morphology

Detailed studies of the morphology were carried out on samples prepared in three ways:

(i) Amorphous sample quench cooled from powder melted at high temperature (nominally 900°C) (Huls), the results of which were qualitatively confirmed on fibres spun at 250°C (RP).

(ii) Compounded at 205°C to eliminate the primary structure.

(iii) Milling the 205°C compound at low temperature (140°C-150°C).

The following table summarises the observations of the Working Party. Initials indicate that that participant observed this structure. The initials with (none) indicates that the participant sought for but did not find the structure, additional comments are also added in parentheses.

Scale of Structure	Test	Amorphous	205°C Compound	Low Temperature Milled
2 nm	Electron microscopy		RP	
10 nm	Electron microscopy	RP, S	RP, S, ICI, M	RP, S
(8-12 nm)	SAXS*	Huls, ICI } (none)	Huls, ICI	
Crystallinity	WAXS*	Huls, ICI } (none)	Huls, ICI	
	DSC*	RP (none)	RP	
100 nm (50-200 nm)	Electron microscopy	ICI	RP (occasional), ICI, CW	S, RP (occasional), ICI
1000 nm	Electron microscopy	RP	RP, ICI, M, S } (none)	

* SAXS - small angle x-ray scattering, WAXS - wide angle x-ray scattering, DSC - differential scanning calorimentry.

(All measurements, except DSC, were carried out at room temperature).

In all cases the structures observed were approximately spherical.

The structure at 2 nm is always seen in electron micrographs of all polymers including known amorphous polymers. Its origin is not understood but it may possibly indicate statistical density variations associated with molecular packing or be an artifact of the measurement. This structure is not thought to be significant in the flow of PVC.

The 10 nm structure (Figure 2-4) has been studied by electron microscopy using a wide variety of sample preparation techniques including: fracture surfaces, solvent and ion etching, and swelling with monomers. Whatever the disadvantages of the different methods of preparing samples all methods appear to indicate the same structure and the Working Party identified this structure as existing in unplasticised PVC. Although the 10 nm structure is on the same scale as the major density fluctuations associated with crystallinity the fact that the structure is preserved when the crystals are melted out, and that it is enhanced by plasticisation(2), allows us to conclude that though the crystallinity may depend on the 10 nm structure the converse is not the case. The Working Party also noted in passing the similarity in scale with the random coil molecule: it is possible that a large number of chains may have their initiation sites close together and in growing together these may produce a morphological feature on the same scale as the random coil whether crystallinity is present or not. The origin of the 10 nm structure remains unclear.

The existence of the 100 nm structure has less decisive support. One participant (RP) always sees occasional features on this scale while two others (ICI, CW) see it as the dominant structure - Figure 5. A fourth participant (S) notes that structures at this scale become coherent after working the sample at low temperature - Figure 6. (Solvay note that the fact that they do not see the structure in the original compound does not mean that it is not present, only that it is broken down by their method of sample preparation). With these conflicting observations it seems probable that the visibility of the structure depends significantly on the method by which the electron microscope specimens are prepared: the structure appears to be most visible when fracture surfaces are studied and particularly when such surfaces are etched; swelling with monomer and microtoming appear to break down or blur the structure. The observation that the structure is intensified - or even created - by shear at low temperature (S) mirrors Geil's observations that such structures are possibly formed by mechanical working(1): further where two structures are present, with the smaller structure contained within the larger, as is the case here, the larger structure is more likely to be the flow unit. That observation strongly suggests that the 100 nm structure will be important in the flow process.

The presence of a memory of primary particles in the amorphous sample serves to emphasise the persistence of all types of structure through simple heat treatments and indicates the importance of mechanical work as well as heat in eliminating the primary structure from the compounds.

Rheology

Seven laboratories (BASF, RP, S, M, ICI, BW and Huls) supplied capillary flow data from which the rheological properties were deduced. The range of such data indicated a standard deviation of 20% in terms of the reproducibility of capillary flow measurements at a given shear rate between difference laboratories, in which respect it is qualitatively similar to a previous collaborative exercise of this kind with PVC of lower molecular weight which showed a standard deviation of 10% between laboratories(4). The lower reproducibility in this case is attributed to the greater difficulty of working with polymers of higher molecular weight, and the less well lubricated and stabilised sample used in this study. Internal comparisons of the flow showed very good reproducibility in that all participants found the suspension polymer to be between 10 and 20% more viscous than the bulk polymer. Those differences were substantiated by dynamic measurements (RP, S). The rheological properties were typical of this class of thermoplastic, showing very strong pseudo-plasticity. Extrudate quality for the 205°C compound was satisfactory in high temperature extrusion but poor in low temperature extrusion.

Four participants (BW, ICI, RP, S) studied the influence of thermomechanical history. The consensus of the results is that shear at low temperature leads to a slight increase in viscosity, as measured from the pressure gradient in capillary flow. This result is attributed to a loss of lubricant after working at low temperature(S). However, more important than any quantitative aspect of the flow is the influence of milling at low temperature on the quality of the extrudate. Figure 7 shows the extrudate obtained after extrusion at 170°C at a nominal shear rate of 10 sec^{-1} through an orifice die. The 205°C compound is barely coherent while the milled sample shows only occasional fissures. These results indicate that low temperature milling alters the flow mechanism in PVC compounds and, in conjunction with the evidence that low temperature milling enhances coherence of the 100 nm structure suggests that it is that structure which represents the principal flow unit.

Deformability of the Flow Unit

The simple indentification of the flow units leaves an incomplete picture as to how these might interact in the flow and further experiments were conducted to assess whether the structural units were themselves deformable.

One laboratory (ICI), using the bulk polymer, compounded at 205°C and milled at 140°C, extruded at 170°C and a nominal shear rate of 50 sec^{-1} and then drew the extrudate 2.5:1 as it cooled. A second participant(S) extruded the suspension polymer at 215°C and drew the extrudate 6:1. Thus two samples were prepared drawn at high and low temperature. The mechanical orientation of these samples was judged by remelting them at 215°C and observing the reversible draw.

	Draw Ratio	Reversible Draw
Low temperature	2.5:1	2:1
High temperature	6:1	2:1

A reversible uniaxial draw of 2:1 on a homogeneous sample indicates that spherical elements should be deformed to ellipsoids with a ratio of 2.8:1 between the lengths of the principle axes along and across the draw direction.

Both participants studied electron micrographs of these oriented samples and concluded that neither the 10 nm nor the 100 nm structure had changed its spherical shape (Figs 8-10). One particpant (ICI) did however observe that in the case of the low temperature drawn sample the 100 nm structure shows a substantial alignment into fibrous strings (Figures 9, 10).

These results indicate that neither the 10 nm nor the 100 nm structure is deformable of itself but that the connective tissue between the 100 nm domains is highly deformable.

CONCLUSIONS

The evidence available to the Working Party is consistent with the flow unit of unplasticised PVC being an approximately spherical domain of about 100 nm diameter which is not itself deformable during processing. The internal structure of these units is composed of an agglomeration of structures on the 10 nm scale. The structure at 10 nm is held together internally by "crystallinity" acting as cross-links(5). The cohesion of the 100 nm structures is increased by working at low temperature. The connective tissue between the 100 nm structures appears to be highly deformable.

Acknowledgement

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2. C Singleton, J Isner, D M Gezovich, P K C Tou, P H Geil and E A Collins Polym Engng and Sci 14, 5, 371 (1974).
3. W Wenig, J Poly Sci (Polym Phys) 16, 1635 (1978)
4. J L S Wales, J Poly Sci Symposium No 50, 469 (1975)
5. H Munstedt, J Macromol Sci Phys B 14, 2, 195 (1977)

APPENDIX I : SAMPLES AND COMPOUNDING HISTORY

Emulsion polymer:	'Vestolit' E6507	(Huls)
Suspension polymer:	'Solvic' 268A	(S)
Bulk polymer:	'Lucovyl' GB1150	(RP)

COMPOUND A (ICI)

The samples were compounded using a standard formulation of stabiliser (3 phr Tribasic Lead Sulphate) and lubricant (1 phr Lead Stearate) in a Bridge type 'BR' Banbury mixer at 116 rpm for 1 minute and 155 rpm for approximately 3 minutes to achieve a melt temperature of $205^{o}C \pm 2^{o}C$. These samples were then granulated. The samples were checked optically to ensure that the primary particles had been eliminated.

Unfortunately using this compound it was not possible to establish conditions by which the emulsion polymer could be rid of its primary structure without incurring an unacceptable degree of degradation. The samples in compound A were thus reduced to the suspension and bulk polymers only.

COMPOUND B (BW)

Samples of each polymer containing 1.5 phr 'Irgastab' T36, 1.0 phr Adwavax 280 and 2.0 phr Loxiol 660, were compounded on a laboratory twin screw extruder at $200^{o}C$.

APPENDIX II : MOLECULAR WEIGHT MEASUREMENTS

Measurements by gel permeation chromatography on original powder samples

Polymer	Participant	$\bar{M}_W$	$\bar{M}_N$	MWD
Suspension	M	82,000	42,000	1.9
	Huls	78,000	35,000	2.2
Bulk	M	76,000	41,000	1.9
	Huls	74,000	34,000	2.2
Emulsion	M	104,000	32,000	3.3
	Huls	83,000	29,000	2.9

Measurements were also made on the two compounds (M) which indicated that while the Banbury compound, A, was substantially the same as the original powder the twin screw extruded compound, B, was of higher molecular weight.

	Weight Average Molecular Weight		
Polymer	Powder	A	B
Suspension	82,000	82,000	88,000
Bulk	76,000	75,000	84,000
Emulsion	104,000	-	100,000

APPENDIX III : THE DIFFERENCES BETWEEN EMULSION AND SUSPENSION AND BULK POLYMERISED PVC

The differences between the emulsion polymer and those polymerised using suspension and bulk technologies is summarised below.

Test	Participant	Relative to the other polymers the emulsion polymer has
Molecular weight $\bar{M}_W$ / $\bar{M}_N$ Distribution	M Huls	higher / lower / broader } Appendix 2
Crystallinity (3) WAXS	BP	lower by factor two
	Huls	lower by factor three
SAXS	Huls	no peak in intensity versus angular displacment plot (figure 1)
Electron Microscopy	RP ICI	primaries still present
Thermal Stability	M BW	poor stability
Viscosity (capillary flow and dynamic studies)	RP M BW S	lower by factor two at all shear rates and frequencies (10^{-1}-1000 sec^{-1}) and temperatures (140-200°C

BP further notes that the twin screw extruded sample of suspension polymer contained two populations of granules varying in crystallinity by a factor of two. This variation was not present in the Banbury compounded samples.

The lower viscosity of emulsion polymers is commonly found when comparison is made between emulsion and bulk or suspension polymers of the same molecular weight but the reason is not understood. For wholly amorphous polymer melts we usually associate viscosity with weight average molecular weight and the fact that the emulsion polymer is of substantially higher weight average molecular weight but lower viscosity is a strong indication that the flow mechanism of PVC is not determined by the usual molecular mechanisms. The Working Party considered the following possible mechanisms to account the different viscosity behaviour.

(i) The presence of some memory of the primary particles eases the flow. While primary particles do undoubtably ease the flow the Working Party was of the opinion that the magnitude of the difference in viscosity was too great for this to be the principle cause.

(ii) The lower 'crystallinity' means fewer effective cross-links in network. If this mechanism were correct the Working Party had anticipated that the viscosity results should converge at high temperature. There is no such trend up to 200°C.

(iii) The low molecular weight tail acts as a lubricant between the flow units or at the wall of the rheometer. Lubricants are known to have a dramatic effect in reducing the 'viscosity' of PVC and the Working Party concluded that this is the more probable mechanism.

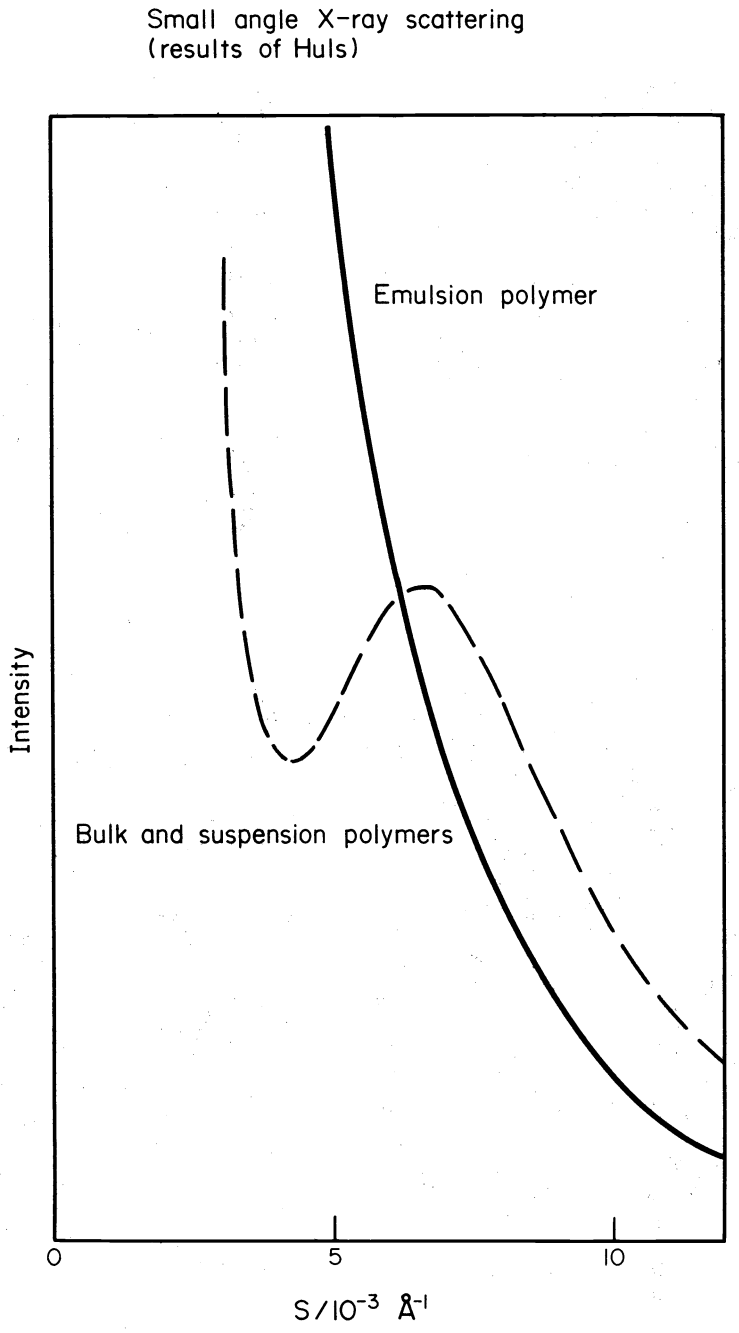
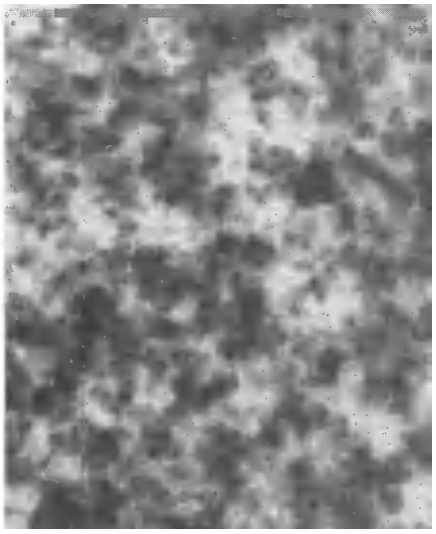

Small angle X-ray scattering
(results of Huls)
Emulsion polymer
Bulk and suspension polymers
Intensity
0
5
10
S/10⁻³ Å⁻¹

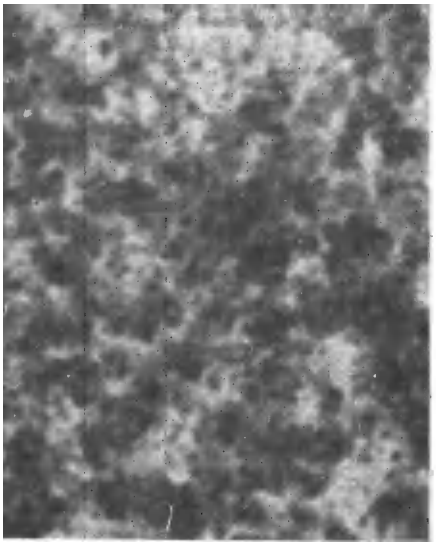
FIGURE 2

Solution polymerised sample, swollen with methyl methacrylate (RP) Magnification 100,000 x (1 mm ~10 nm).

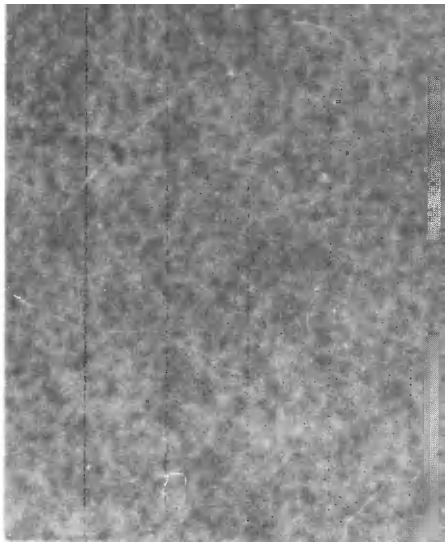
Sintered powder (200°C)



Banbury compound



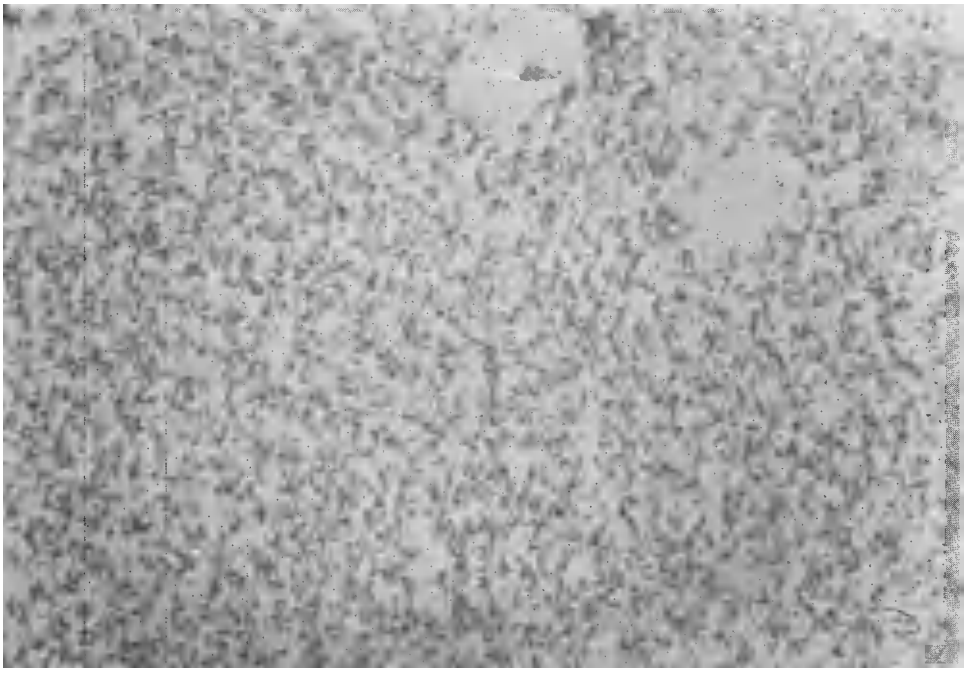
Banbury & Brabender at 150°C



Banbury & RMS at 230°C

FIGURE 3

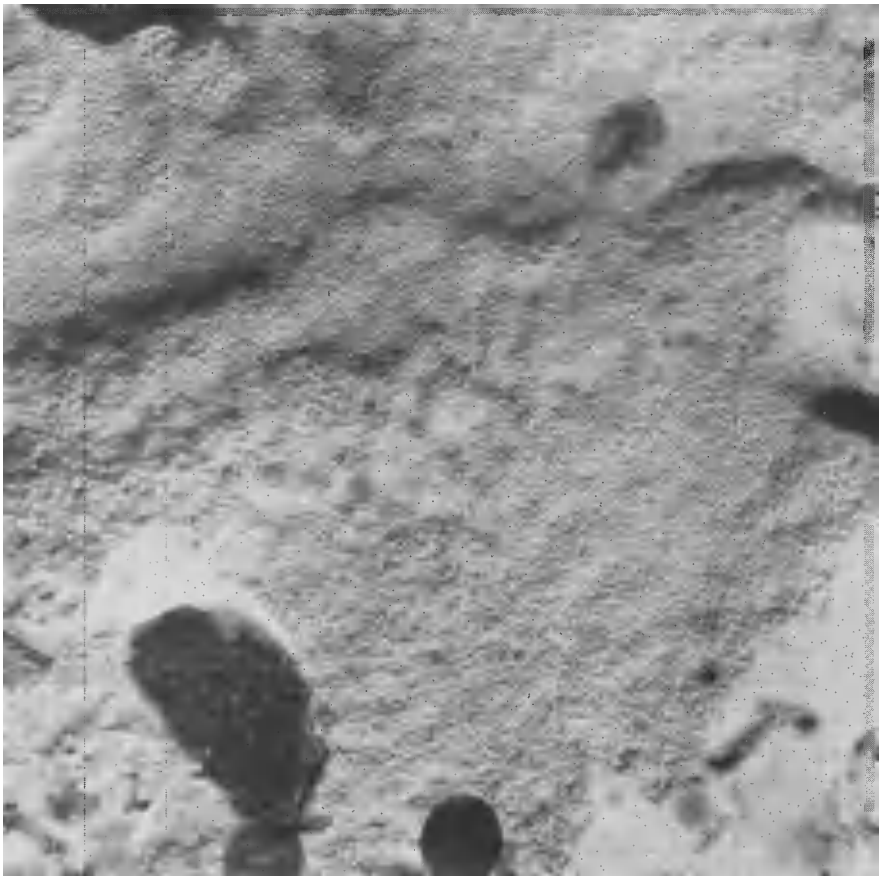
Bulk polymerised PVC compounded at 205°C, swollen with methyl methacrylate (S) Magnification 20,000 x.



→|←
100 nm

FIGURE 4

Bulk polymerised PVC compounded at 205°C, ion etched (ICI)
Magnification 46,000 x.



→| |←
100nm

FIGURE 5

Bulk polymerised PVC compounded at 205°C, milled at 140°C and extruded at 170°C - fractured surface (ICI) Magnification 32,000

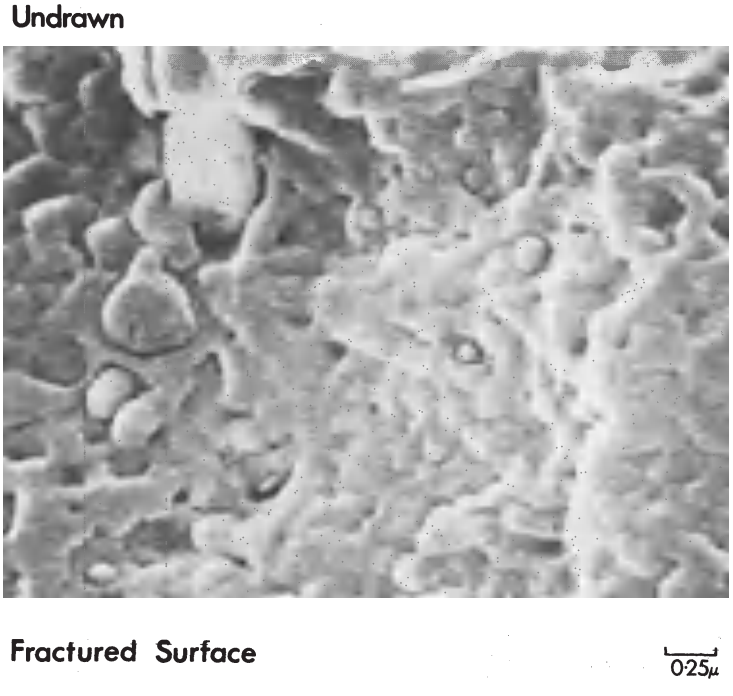
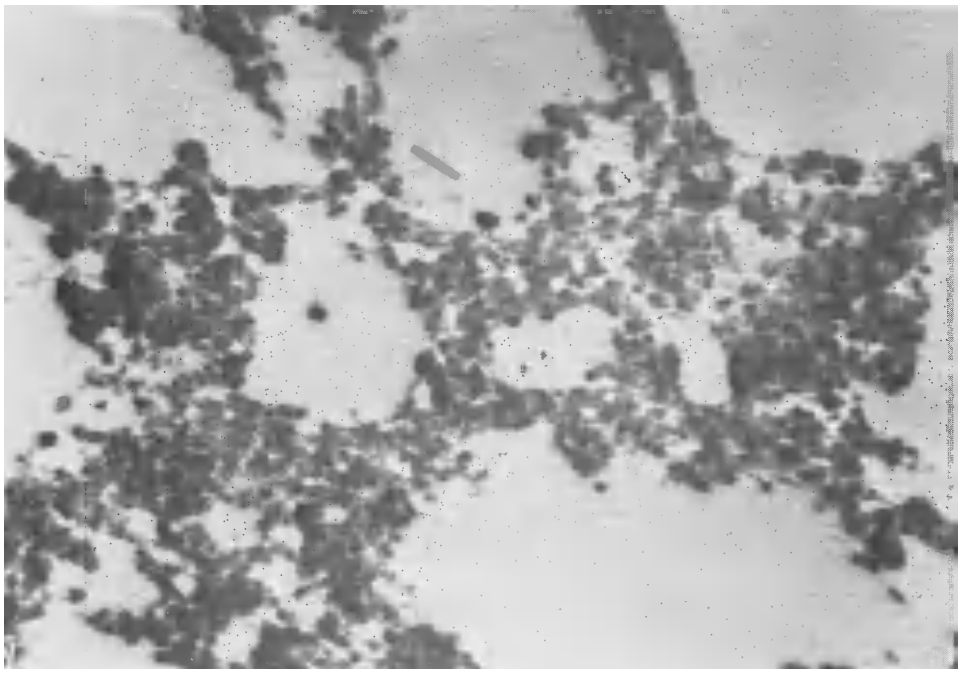


FIGURE 6

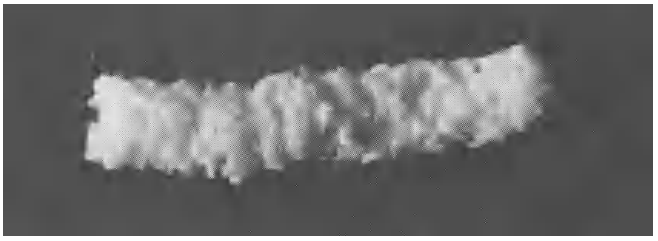
Bulk polymerised PVC compounded at 205°C milled at 140°C - swollen with methyl methacrylate monomer (S) Magnification 20,000 x.



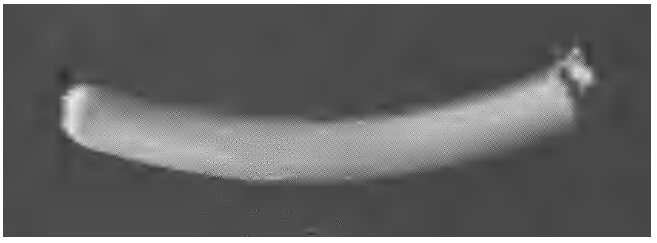
compare with Figure 3

FIGURE 7

Samples extruded at 170°C through a 4mm diameter orifice at a nominal shear rate ($4Q/\pi r^3$) of 10 sec^{-1} (ICI)



205°C COMPOUND

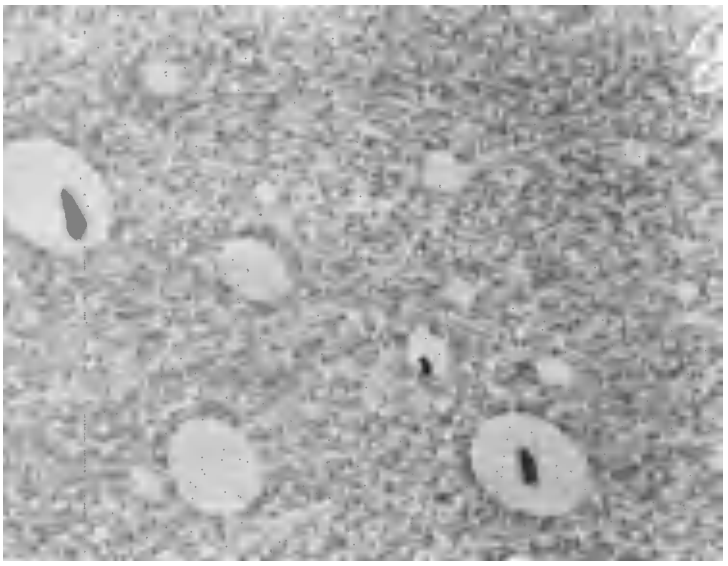


COMPOUND MILLED AT 150°C

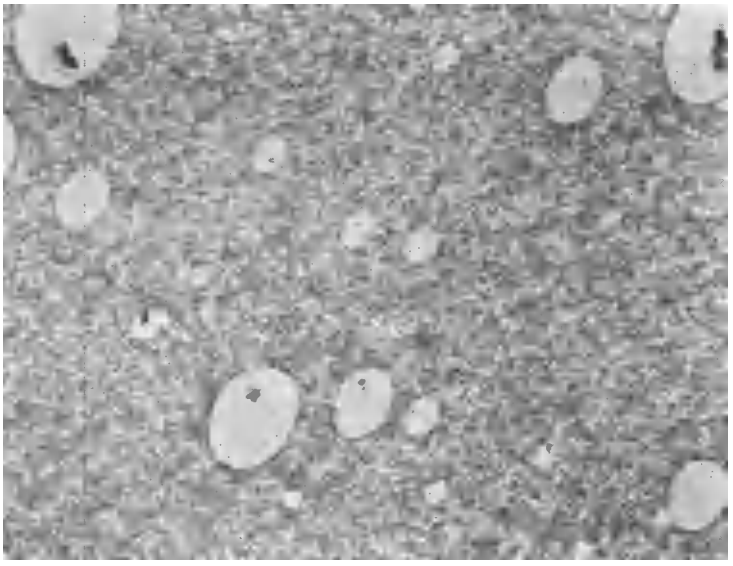
10 mm

FIGURE 8

Solution polymer compounded at 200°C and extruded at 215°C - swollen with methyl methacrylate monomer (S) Magnification 20,000 x



undrawn

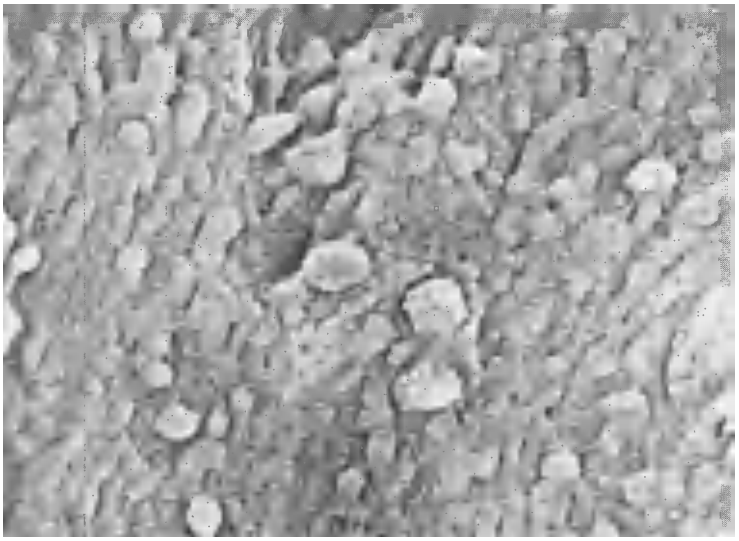


drawn 6:1

FIGURE 9

Bulk polymerised sample compounded at 205°C, milled at 140°C and extruded at 170°C - fracture surface (ICI) Magnification 32,000 x

Drawn 2·5 : 1



Fractured Surface

0·25μ

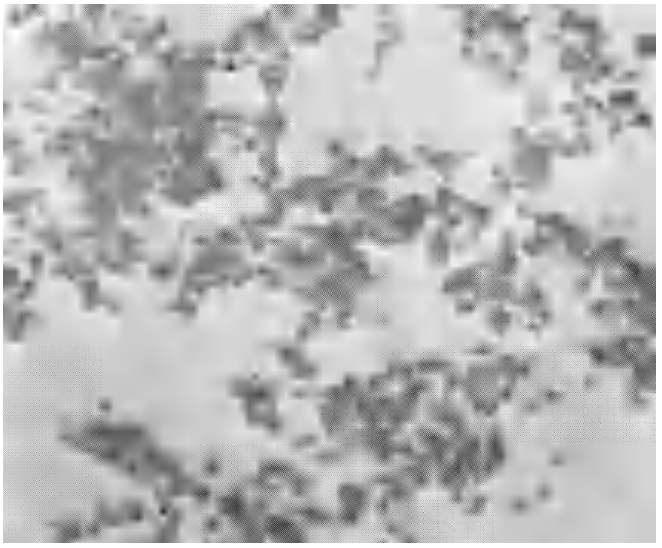
For undrawn sample compare figure 5

note stringing of particles

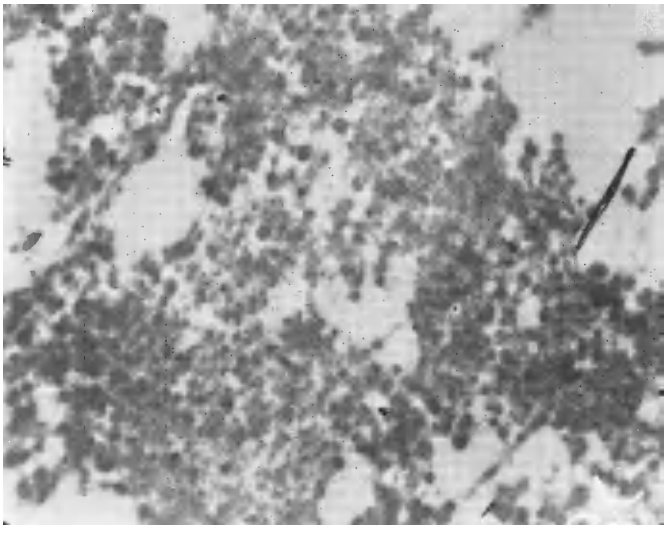
FIGURE 10

Bulk polymerised sample compounded at 205°C, milled at 140°C and extruded at 170°C (ICI) - swollen with methyl methacrylate monomer (S)

Magnification 20,000 X



undrawn



drawn 2.5:1