PARTICULATE NATURE OF PVC

Formation, Structure and Processing

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APPLIED SCIENCE PUBLISHERS LTD
LONDON

APPLIED SCIENCE PUBLISHERS LTD
RIPPLE ROAD, BARKING, ESSEX, ENGLAND

British Library Cataloguing in Publication Data

Particulate nature of PVC.
1. Polyvinyl chloride
I. Butters, G.
668.4′236 TP1180.V48

ISBN 0–85334–120–6

WITH 15 TABLES AND 90 ILLUSTRATIONS

Photoset in Malta by Interprint Limited
Printed in Great Britain by Galliard (Printers) Ltd, Great Yarmouth

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Preface

Although all the major thermoplastics can exist in powder or granule form the particulate nature of poly(vinyl chloride) (PVC) is unique in the extent to which it can influence compounding and processing technology. This book concerns this important feature of PVC, dealing with the production, properties, structure and processing from the standpoint of the PVC powder particle.

PVC powder consists of particles which themselves are composed of at least two smaller particulate species. In this book the authors designate these species according to the system proposed by Faulkner (Chapter 1, ref. 1) in which the initial particulate structure formed during polymerisation is designated the Stage I particle. Stage I particles combine to form Stage II particles which in turn combine to form Stage III particles (*ca.* 130 μm) which are the final particles constituting suspension and mass polymerised PVC powders. The attraction of this system over the others described in the first chapter is its simplicity.

In the first two chapters, Clark describes the industrially important polymerisation processes, the mechanisms of particle formation, the physical structure of the particle and the characterisation of the basic particle and bulk powder properties. The third chapter is concerned with the molecular structure of the polymer chains which make up the Stage I particle and which generally remain substantially unchanged in the final fused product. The fourth and final chapter is concerned with the influence of the particulate nature on bulk handling, interaction with additives, compound formulation and preparation and processing including an in depth study of the nature and measurement of the fusion process viewed as the successive breakdown of the Stage III, Stage II and Stage I particulate species.

Although much of the subject matter is dealt with from the standpoint of particle technology, the book nevertheless is a detailed and broad study of the production, properties, structure and processing of PVC and is intended for all having an interest in these aspects of PVC technology, especially scientists and engineers in industry or academia.

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Acknowledgements

The editor and authors are indebted to many who assisted in the preparation of this book and the following is by no means a complete list. Susan Clark, the wife of one of the authors, prepared the figures for Chapters 1, 2 and 4. Several colleagues helped in a variety of ways and particular mention must be made of F. J. Bellringer, F. P. Gintz, J. M. Cann and A. R. West who read the manuscripts and made helpful comments, Linda Evans and T. J. C. Sleeman who prepared most of the photographs and Joan Bowles and Mary Bailey who typed the manuscripts. Finally, thanks are due to BP Chemicals Limited and the British Petroleum Company Limited for their permission to publish this book and for providing the necessary facilities for its preparation.

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Chapter 1

Particle Formation

M. CLARK

1.1 INTRODUCTION

Poly(vinyl chloride), commonly known as PVC, was first recognised and characterised more than 100 years ago but, due to its poor thermal stability making processing difficult, it was not until about 1930 that it started to gain commercial importance. The problems caused by poor thermal stability were overcome by the development of suitable stabiliser systems and PVC is now one of the world's leading synthetic polymers with a total world production capacity in 1979 approaching 15 million tonnes. Commercial manufacture is now mainly by the suspension, mass, emulsion and microsuspension routes.

The suspension and mass polymerisation processes both produce a particulate, free flowing product having the same general appearance with a mean particle size usually in the range 100–150 μm. The microsuspension, and more especially the emulsion process, produces a product having a very small and narrow particle size distribution of the order 0·1 to 2 μm when in its latex form. The latex is normally spray dried, causing agglomeration and formation of a particulate product having a wide range of particle size from 0·1 μm up to 100 μm. All PVC products, however, have a series of particulate sub-structures.

Suspension and mass polymers are usually porous in nature and, although there are detailed differences in their surface appearance, it is easy to see by either cutting open or thin sectioning a single particle (see Fig. 1.1) that they are both made up of a large number of much smaller

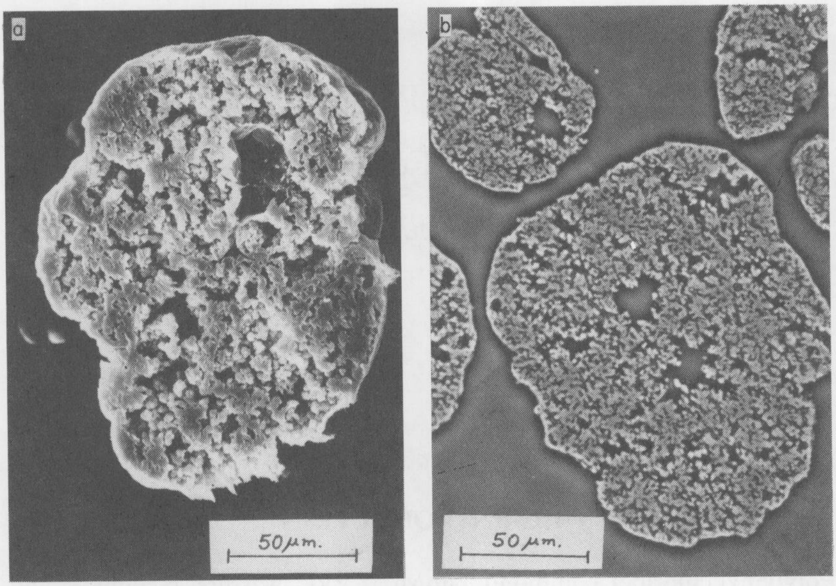

Fig. 1.1. Suspension PVC single Stage III particle (a) cut open and viewed by SEM (b) embedded in epoxy resin, microtomed and observed by optical microscope.

particles. Using the terminology proposed by Faulkner,[1] as will be done throughout this book, these approximately 1 μm diameter entities will be called Stage II particles with the complete grain being referred to as a Stage III particle. Many other different terminologies have been used with Stage II particles, the importance of which have been recognised for some time,[2,3] often being called microgranules or primary particles.

In Fig. 1.1 the Stage II particles can be seen to be partially fused together to form a three dimensional lattice thus giving the structure strength and rigidity. Some workers have referred to sub-particles intermediate between those of the Stage II and Stage III particles but it is likely that such observations refer to well fused agglomerates of Stage II particles.

In the case of emulsion and microsuspension processes the polymerised latex particle size is of the same order as the Stage II particle seen in the mass and suspension grains and can be equated to it. Powder product obtained after spray drying consists of sintered agglomerates of the latex particles with a range of size of approximately 0·1–100 μm and a mean of about 40 μm although subsequent grinding, substantially reducing this particle size, is usually employed. These agglomerates can be considered Stage III particles.

In probably all three resin types the Stage II particles are themselves made up of even smaller particles. The number of different types of sub-Stage II particles claimed varies from one[3] to up to four[4] while observations by other workers[5] appears to deny their existence at all.

Hattori *et al.*[3] using a methylmethacrylate embedding technique, found the presence of sub-micron structures in polymerised and extruded suspension PVC. They reported the presence of fibrillar structures at the 100–300 Å level and put forward a scheme (Fig. 1.2) for a suspension PVC granule (Stage III particle).

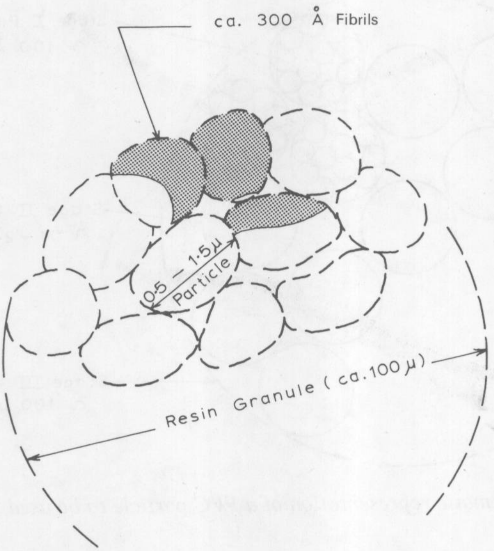

Fig. 1.2. Structure of suspension PVC granule as proposed by Hattori et al.[3]

Subsequent workers[1,6] have proposed very similar structures although detailed description of the *ca.* 300 Å particle differ somewhat. These particles will be referred to as Stage I particles as they are believed to be those initially formed in the polymerisation process. They are now most commonly quoted as being of about 100 Å diameter.

Some workers have also reported particles about 1000 Å in size although their presence in all circumstances is not proven. Geil[7] suggests that such 1000 Å structures might be formed by mechanical working within or from 1 μm Stage II particles.

For the purpose of the present chapter fine structure in the crystallographic sense, which is thought to feature in the 100 Å Stage I's, will be disregarded. The nature and factors affecting such a fine structure are considered in Chapter 3.

Thus as a basis for the discussion in the rest of this chapter the following, possibly simplified, structure and terminology will be used for describing the microstructure of PVC (Fig. 1.3).

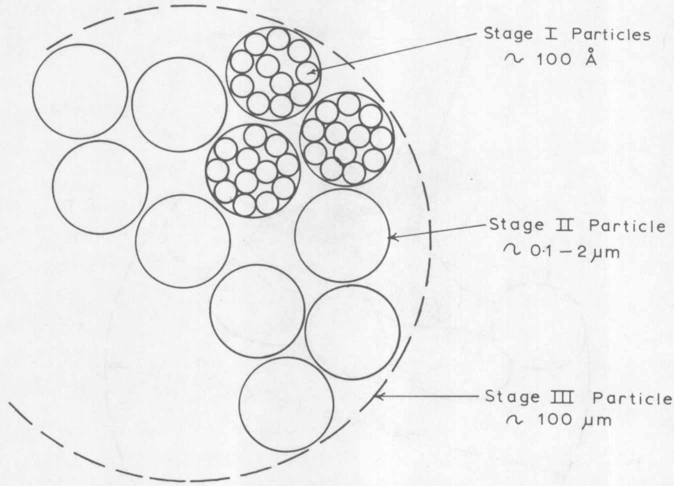

Fig. 1.3. Schematic representation of a PVC particle to be used in the text.

This chapter will take each of the three major PVC manufacturing processes in turn and, after a brief description, highlight the production parameters that can be used to control the particulate and morphological characteristics of the products.

1.2 SUSPENSION POLYMERISATION

1.2.1 General Description of the Suspension Polymerisation Process

By far the majority of PVC is produced via the suspension route. In this