

PVC TECHNOLOGY

by
W. S. PENN

Third Edition



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Revised and Edited by

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APPLIED SCIENCE PUBLISHERS LIMITED
LONDON

PREFACE TO THE THIRD EDITION

The task we were originally set was to revise the book in the sense of bringing up to date the information it contained. We have done our best to achieve this. Having no brief to re-cast it completely we have retained the original concept, scheme, plan and pattern of the work; these, together with a considerable proportion of the text which we left without substantial alterations, still stand fully and entirely to the credit of the late Author.

However, we have also tried — within certain stipulated space restrictions — to add something to the true technological content of the book. To this end we have largely re-written some of the chapters (chapters 1, 5, 11, 16, 18, 24, 28 and 29), and revised certain others fairly extensively. We have also revised, amended and augmented the literature references in most chapters. Finally, we have replaced many of the original illustrations and added two Appendices. Appendix 1 is a specially compiled, extensive list of international and national specifications (British, German and American) relating to material standards and standard test methods for pvc and products therefrom. Appendix 2 contains conversion factors and definitions of units. Apart from such matters as the arrangement and presentation of the material, the nature and effect of the changes we have made are our responsibility.

W.V.T.

B.J.L.

ACKNOWLEDGEMENTS

First and foremost, it is with real pleasure that we acknowledge our indebtedness, and record our grateful thanks, to Mrs Irene Chizlett who alone carried the considerable burden of all secretarial work associated with the undertaking, typed and collated the script, and helped in innumerable other ways.

On the technical side we have received information and help from many organisations and individuals. The principal aim of the revision of this book was to bring the information it contains up to date. A substantial proportion of the information is, at least partly, commercial (manufacturers' price and property data on their products). It was, therefore, necessary to ask many companies for current information. In almost all cases the response was extremely helpful, and we would like to thank all the companies who responded in this way; they are all those whose products received more than a passing mention in the original editions of the book and remain in this position in the present revised edition.

Apart from help towards more or less straightforward revision of available data, we have also been the recipients of other help towards making the book more useful to the reader. In this connection we would like to thank the following of our colleagues at the Yarsley Laboratories: Messrs. G. C. Ives, J. A. Mead and M. Riley, for helpful advice and for certain data on international and British Standard specifications, Messrs. D. J. Trafford and D. B. S. Berry for information on certain test methods, Mr L. W. Turner, for valuable comment in connection with the revision of the chapter on injection moulding, Mr J. A. Shelton for items of statistical information originally published in '*Polymeric*s', and Mr I. Atkinson for taking the IR spectra reproduced in Chapter 1.

We are also particularly grateful for helpful discussions and advice to Mr T. C. Moorshead of Albright and Wilson Ltd., Oldbury Division, and Messrs. H. Webber, K. T. Collington, P. W. Jones and C. M. Lavender of Fisons Industrial Chemicals Ltd.

Our special thanks are also due to the following people who actually contributed a few sections: Mr P. R. Grindley, ICI Ltd. (Section 7.5.1, Hexaplas plasticisers), Mr H. G. White, ICI Ltd. (Section 13.6, Commercial Pigments, and also comments on our script of Section 13.5), Mr R. F.

Godfrey, ICI Ltd. (Section 7.7.1, Chlorinated paraffins), Mr R. W. Berman, Welwyn Tool Co. Ltd., (Section 21.3.1, Hot air and gas welding).

In compiling his chapter on pvc latices (Chapter 26), the late Author utilised a lot of information available in the then current edition of the *British Geon Technical Manual* on polymer latices. An expanded and revised version of this manual now constitutes Technical Manual No. 5 (Breon Latices) of BP Chemicals International Ltd. It was our opinion that that publication's section on pvc latices (pages 87-110) is a technically better and more balanced account of the subject than that provided by the late Author of the present book. For this reason we have decided that it would be of considerable benefit to the reader to replace in the revised edition of this book the original Chapter 26 with the above-mentioned 'Breon Latices' section, and we are grateful to BP Chemicals International Ltd. for their permission to do so. Although the chapter now deals with one particular manufacturer's range of vinyl latices, the range provides an excellent example of good products of this type which are available also from other manufacturers.

Messrs. K. Drysdale (Lennig Chemicals Ltd.), D. R. Cox (Durham Raw Materials Ltd.), Dr V. Oakes (Pure Chemicals Ltd.), T. A. Thompson (Shell Chemicals International Ltd.), P. G. Youde and P. Sime (BP Chemicals International Ltd.), C. H. Cornell, P. J. B. Newsom and G. Breach (Vinatex Ltd.), H. Grimshaw (Belgrave Industries Ltd.), D. G. Paull (Associated Lead Manufacturers Ltd.), V. T. Gardner (Bone Craven Ltd.) and C. J. Kershaw (Hamilton Machinery Sales) were also particularly helpful in providing material on their company's products.

Several companies were kind enough to supply plates illustrating various items of modern machinery for processing pvc. Acknowledgement of source is made individually in connection with each illustration, and to all those companies mentioned in this way we would like to record our thanks.

The revised text includes figures and other data reproduced from papers which appeared in various publications. Most of the sources are acknowledged at the appropriate point in the text, but we would like to thank the following for permission to publish some of the items: Mr D. Nield (Lankro Chemicals Ltd.) — Table in Chapter 6, the Editor of *European Chemical News* — material in Tables 1.1 and 2.1, the Editor of *British Plastics* — Table 2.2 and data on creep in thermoplastics, Carl Hanser Verlag, publishers of *Kunststoffe* — Fig. 1 in Chapter 28.

Last, but not least, one of us (W.V.T.) is indebted to Mr H. White and Messrs. James North and Sons Ltd. for permission to refer to, and publish an extract from, work originally carried out on their behalf (investigation into gelation properties of pvc — Section 25.1.2), and to the Yarsley Research Laboratories Ltd., for permission to undertake the revision, and for certain office facilities and other help.

W.V.T.

B.J.L.

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CHAPTER 1

INTRODUCTION

1.1 EARLY WORK ON COMPOUNDS

It is surprising how comparatively recently pvc, in its plasticised form, became a commercial material. Carleton Ellis¹ could still write in 1935 that 'one disadvantage of polyvinyl chloride as a moulding resin is its tendency to decompose at the temperature required in the moulding operation'. The use of stabilisers and plasticisers, as we know them, was almost unknown. However, it was realised that some esters² acted as plasticisers and some alkaline earth metal soaps as stabilisers,³ even though they were not much used.

In those early days, pvc was plasticised with such materials as tung oil,⁴ alkyd resins⁵ and similar products. True plasticisers such as DBP were added more or less as an afterthought² and, in one case, DBP was added to the extent of 11 phr in a coating composition. The impression conveyed is that the infant plastics industry was desperately trying to find some real use for pvc and one suggested⁶ was an adhesive (with rubber and cellulose derivatives) for sticking patches on worn places in clothing!⁷

Some progress was made when it was discovered that copolymers with vinyl acetate moulded more easily. It is now realised that this is internal plasticisation but it was hardly thought of as such then. It may appear surprising that one of the early applications of the copolymers was in gramophone records⁸ where fillers such as silica and mica and a little DBP might have been employed.⁹ Moulded dentures were another important application.¹⁰ In some cases it is possible that a 'rigid' copolymer (with no external plasticiser) was inadvertently being moulded. Thanks to the work of Kaufmann¹¹ the early history of pvc polymers, compounds and processing is now well recorded and documented.

It was World War II that really brought pvc into its own. It was soon realised that plasticised pvc was an effective substitute for rubber in some applications, particularly cable insulation and sheathing. Thus pvc helped to ameliorate the acute rubber shortage and at the same time established itself as a material in its own right. Although some companies reverted to rubber as soon as they could after the war, many did not and pvc grew rapidly in importance. Now it is widely used in many industries and applications.

1.2 EARLY MACHINES

In the pre-war period, and to some extent during the war, pvc processing was largely carried out by methods and on machinery developed for rubber or celluloid. The processes involved were mixing, calendering, compression moulding and extrusion (including wire coating).

The paddle-type Gardner premixers were in use at an early period, but between, say, 1942 and 1945, open mill mixing of the final product was in very common use. As the use of internal mixers was adopted it was soon found that pvc compounds could be readily mixed in them, in spite of contamination from rubber lodged behind rotors.

The open mills (and mixers) had to be used at higher temperatures than usual. Steam pressures were increased at the risk of grease melting extensively and draining away from bearings, and it is surprising how much work was accomplished without damage. Electrical heating, particularly for extruders, was a logical development but one which was fully utilised only slowly. The need to modify the rubber extruders on which early work was carried out at temperatures higher than normal soon became plain, and modifications, e.g. to enable the polymer to be fed in granular form and reliably to provide higher processing temperature (by electrical heating), followed. A special ram extruder was employed in Germany for the production of pvc rigid pipe from a pvc billet.^{1,2} The history and early development of the pvc extruder and other processing machinery have been well described by Kaufmann.^{11,12}

The modern techniques and machines are dealt with in this book.

The development of modern pvc processing machinery and of the many specialised processes which comprise present-day pvc technology has paralleled the remarkable expansion of the volume of pvc production and the scope and number of its applications.

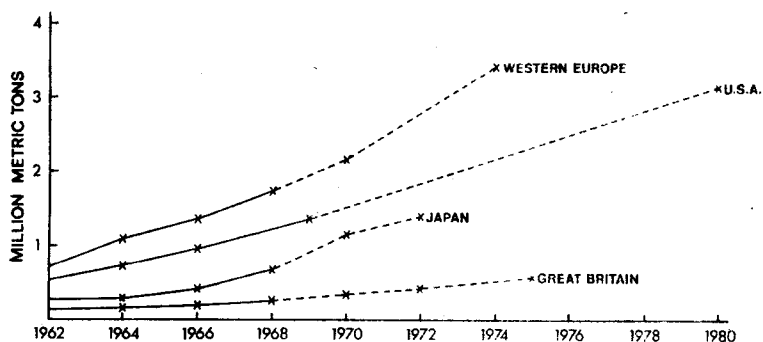


Fig. 1.1 PVC polymer consumption.

1.3 GENERAL STATISTICS

Today pvc is second only to the polyolefins in terms of the amount produced, which represents about 25% of the total production of all plastics, and about 40% of thermoplastics.

Figure 1.1 illustrates the consumption of pvc in the UK, Western Europe (including the UK and Spain), Japan and the USA, which are the most important consumers (as well as producers) of the polymer.

The principal primary uses are shown in Table 1.1 which also illustrates where the main growth has taken place. The Table relates to the UK, but the general pattern has been similar throughout the Western world.

Good regular sources of current statistical and commercial information on pvc include the following: *British Plastics* (current commercial and production statistics for plastics in the UK are provided in the January issue each year); *Modern Plastics* (provides similar information on the position in the USA; and *Polymeric** (Sections A and B contain information on statistics and commercial activities). Some statistics and market information specifically relating to pvc will also be found in the *Plastics Industry Profit Guide* published annually by the Society of Plastics Engineers.

In addition, useful commercial and statistical surveys of the pvc field have appeared in the *European Chemical News*,¹³ and *Courrier d'Europe plastique Eurocaoutchouc*.¹⁴

1.4 OUTLINE OF THE PVC SECTOR OF THE PLASTICS INDUSTRY

Companies operating in the pvc sector of the plastics industry generally fall into one of four main categories, which are as follows:

1. polymer producers;
2. compounders;
3. processors;
4. companies selling finished goods consisting of or containing pvc.

Polymer importers have not been included in this sequence because they do not normally engage in technical activities. They are however, with the producers, members of the more general category of polymer suppliers.

Some companies fall within more than one of the categories listed, for example, the polymer producers all produce compounds; some also produce semi-finished goods. It should be appreciated at this early stage that the number of polymer producers in any country is very small when compared with the large numbers of companies in the other categories. In the UK for instance there are only four polymer producers. Category 4

* This is a monthly world digest of plastics and related technology, published by the Yarsley Research Laboratories Ltd.

TABLE 1.1
*Primary-use 'Breakdown' of PVC Polymer Consumption
in the UK*

PVC type and primary use	Consumption				
	1965	1968	1972 (estimated)		
	'000 metric tons	'000 metric tons	% growth since 1965	'000 metric tons	% growth since 1965
FLEXIBLE PVC					
Calendered sheet and film	33.3	41.0	23.3	58.0	74.3
Cable and wire	35.4	41.0	15.8	55.0	55.2
Coating	12.5	21.2	69.5	32.0	156.2
Flooring	27.1	32.5	31.0	37.5	33.4
Belting	6.2	5.3	-14.5	4.3	-19.2
Footwear	4.1	9.9	141.5	19.5	376
Other extrusions	11.9	14.2	19.3	23.5	97.6
Dipping and slush moulding solution	8.3	11.4	37.4	15.0	80.8
Misc., including foams	4.9	8.5	73.5	11.5	134.6
TOTAL FLEXIBLE	143.7	185.0	28.9	256.3	78.5
RIGID PVC					
Rigid pipe and fittings and profiles	27.1	51.0	88.3	98.0	262
Rigid sheet and film	8.0	11.5	43.8	21.0	162.5
Bottles	1.3	2.3	77	12.0	824
Records	8.8	9.9	12.5	13.0	42.7
Other injection moulding	3.1	7.5	142	17.0	448
TOTAL RIGID	48.3	82.2	70.3	161.0	233
TOTAL RIGID AND FLEXIBLE	192.0	267.2	39.2	417.3	117
RESIN EXPORTED AS COMPOUND	15.6	17.0	9.3	22.0	41
TOTAL MARKET	207.6	284.2	37	439.3	111.7

above will contain many companies for which pvc is but a small part of their interests. Nevertheless, such companies can use very large quantities of pvc and are very important to the industry, e.g. the automobile producers.

The principal processes used to convert the pvc to finished and semi-finished goods are extrusion, calendering, injection moulding and spread coating. Although some companies are concerned with more than one of these processes, most tend to specialise in one process. In some cases the processed pvc is marketed directly by the processor (e.g. unplasticised pvc pipes), whilst in other areas the processor passes on the pvc in semi-finished form to another company which employs the material in its products, e.g. vinyl automobile upholstery.

In addition to the material producers, converters and users, there are many companies which specialise in the supply of additives for use in pvc compounds, e.g. plasticisers, stabilisers, lubricants, fillers, etc. It is relevant to point out that the value of the total market for some of these materials exceeds that of many other plastics materials.

Also worthy of mention — since without them there would be no pvc industry — are the machinery manufacturers. Many companies have specialised in equipment for pvc processing and through their development work on plant and equipment, new applications for pvc have been made possible.

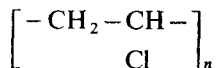
The principal areas of application of pvc are indicated in Section 1.3. It may also be noted in passing that the building industry is the most important user of pvc, particularly unplasticised pvc.

1.5 PVC AND VINYL CHLORIDE COPOLYMERS — GENERAL

1.5.1 *PVC: Main Properties*

Chemical Structure and Morphology

The fundamental repeating unit of the pvc chain is

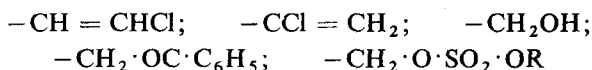


In commercial resins, n (the degree of polymerisation) may have values between about 500 and 2000; i.e. the molecular weight range is, roughly, 30 000–100 000 plus.* PVC of much higher molecular weights has also been made.

The nature of the terminal groups of the pvc chain varies with the method

* These figures differ somewhat from those in Table 2.2(a). This is because in practical determinations the molecular weight and degree of polymerisation figures depend on the method used. True average molecular weight lies between the weight-average and the number-average values.

of production (suspension, emulsion, bulk or solution polymerisation — cf. Chapter 2), and any of the following may be present:



(where R = alkyl). In commercial pvc polymer the chains are branched, estimates of the degree of branching varying from 0.2–2.0 branches per 100 carbon atoms.¹⁵

Commercial polymers normally give diffuse X-ray diffraction spectra, and — mainly on this and infra-red spectral evidence — are considered to be substantially amorphous ('% crystallinity' not more than 5%).^{16,17} Crystalline stereoregular pvc has also been prepared^{15,18} (by radical polymerisation at low temperatures) and used in the production of pvc fibres and film.¹⁹ The chains of the crystalline polymer are more highly linear than those of the conventional pvc resins; in comparison with the latter, crystalline pvc is also higher-softening, more resistant to solvents, stronger, and has lower creep. The modulus is also higher, but the impact strength is lower.^{15,18,19} Typical infra-red spectra of unplasticised and plasticised pvc are given at the end of this chapter.

Physical Properties

These are very strongly dependent on the nature and type of plasticisers present, and — albeit to a much lesser extent — also on other compounding ingredients. The following data illustrate some of the important properties of commercial pvc.^{16,20}

	<i>Unplasticised</i>	<i>Plasticised</i>
Specific gravity	1.4	down to about 1.25
Water absorption	<0.5%	up to 0.5%
Tensile strength*	about 6 kg mm ⁻²	down by a factor of 4 or more
Elastic modulus	150–300 kg mm ⁻²	down by a factor of 100 or more

* The tensile strength values are considerably higher for pvc fibres, in which the polymer is oriented by stretching.

Chemical Properties

These are also affected by the presence of plasticisers, albeit to a lesser extent than the physical properties. 'Pure' (unplasticised) pvc is resistant to most acids and alkalis, although it is decomposed by concentrated sulphuric, nitric and chromic acids. It is dissolved by tetrahydrofuran and

isophorone, swollen to varying extents by ketones, esters and aromatic and chlorinated hydrocarbons, but is resistant to aliphatic hydrocarbons and oils.

Some chemical resistance data are quoted in Table 22.8. A comprehensive list, covering both plasticised and unplasticised pvc, has been published by ICI Ltd.²¹

Miscellaneous Properties

Glass transition temperature (T_g): conventional pvc — about 80°C; crystalline pvc — up to about 110°C, depending on temperature of polymerisation.¹⁵ Plasticisation lowers the effective T_g (cf. Chapter 5), and hence the softening point and heat distortion temperature.¹⁵ The melting point of crystalline pvc may be as high as 273°C.¹⁵

The electrical properties are strongly affected by plasticisation.

Many of these, and other properties, are discussed further in the relevant chapters and sections of this book.

1.5.2 Copolymers of Vinyl Chloride

Some vinyl chloride copolymers are long-established materials. Others, more recent, have also become of more than academic interest, some entering the commercial field. The main copolymers are listed and briefly described in Table 1.2.

Introduction of a comonomer into pvc normally permits lower temperatures to be employed in thermal processing; such processing is thus made easier and the risk of decomposition — always a factor with pvc — can be minimised without resort to external plasticisers (cf. also Chapter 5). In some cases physical properties (and hence performance in service) may be improved; solubility is also normally increased by the presence of a comonomer in the pvc chain.

With the exception of the acrylic and modacrylic fibres, in which the maximum vinyl chloride content can be respectively 15 and 65%, all the above copolymers will normally contain about 80% or more vinyl chloride. They are also all copolymers in which all the comonomer units are in the main polymer chain.

Graft copolymers have also been produced and patented^{19,25} including vinyl chloride grafted on to polyolefins (Montecatini), vinyl chloride grafted on to ethylene/vinyl acetate copolymer (Bayer and Dynamit Nobel), and vinyl chloride grafted on to butadiene/acrylic ester copolymers (Pechiney-Saint-Gobain). The graft copolymers provide alternatives (albeit rather expensive) to the main-chain copolymers and blends, where improvements in processing properties and transparency are desired. The graft copolymers may also be blended with the homopolymer to achieve similar results.

TABLE 1.2
Vinyl Chloride Copolymers

Copolymer	Main applications	Remarks	References
Vinyl chloride/vinyl acetate	Solution applications; unplasticised mouldings and sheeting; gramophone records. Fibres (<i>e.g.</i> Vinyon HH — American Viscose Corp.) are also produced from this copolymer	For commercial resins and applications <i>cf.</i> Chapter 2, Sections 2.4 and 2.5 and Chapters 27 and 29	<i>e.g.</i> 16 and 20. Literature on this copolymer is extensive
Vinyl chloride/vinylidene chloride	Unplasticised calendered products; viscosity-reducing polymer in pastes; solution; fibres and filaments (Saran* — National Plastics Products Co.)	Commercial resins: <i>cf.</i> Section 2.5 and Chapter 29	16, 20
Vinyl chloride/acrylonitrile	Fibres (vinyl chloride is the comonomer in acrylic and modacrylic fibres, <i>e.g.</i> 'Dynel' — Union Carbide Chemicals Co.)	<i>cf.</i> Chapter 29	20