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Polyvinyl Chloride and its Organotin Stabilizers with Special Reference to Packaging Materials and Commodities: a Review*

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Polyvinyl chloride (PVC) is a thermoplastic that has entered practically all areas of life as a cheap and versatile material. Since PVC also fulfils the high quality requirements placed on modern packaging materials, with respect to packaging techniques and consumer protection, it is being used to an increasing extent for packaging of food and beverages as well as pharmaceutical and cosmetic products. The various additives required for processing PVC into packaging materials and commodity articles, as well as improving its properties during usage (e.g. lubricants and stabilizers), are harmless with regard to human and ecotoxicological aspects. Their use is non-hazardous and is therefore permitted by authorities. In the group of thermo- and light stabilizers for PVC, mixtures of mono- and dialkyltin thioglycolates play a major role. In accordance with legislation, these are allowed to be used in rigid PVC. In addition to their excellent stabilizing effect, they are not hazardous to the health of consumers of products packed in rigid PVC.

Similarly, no health hazards exist to personnel, working in PVC production and processing plants, from volatile components of organotin stabilizers provided that processing and environmental prerequisites of modern technology are observed. The disposal of household waste that contains used PVC materials — stabilized with mixtures of mono- and dialkyltin thioglycolates — does not cause additional difficulties.

Keywords: PVC; organotin stabilizers; ecotoxicology; packaging materials; waste disposal

PART I — INTRODUCTION

Plastic materials have entered practically all areas of technology, in commercial and daily life. Thereby because of superior properties and a broad spectrum of characteristics and economic advantages, plastics have been able to displace and/or supplement traditional materials, such as wood, glass and metal. It is certain that they will continue to play an increasingly significant role in future. This is indicated, for instance, by progress in the development of electrically conducting and fireproof polymers, which can be used in the electrical and electronics industries and for fire-proofing technology. Thus, expensive and non-replenishable resources like copper, silver

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and special metal alloys, as well as less suitable fire-proofing materials, can be substituted by plastics. The development of novel polymers would find increasing application of plastics in other technical areas.

This versatile and still expanding field of plastics application, if evaluated objectively, contributes towards improved living conditions of modern society by, for example, providing cheap consumer articles and household utensils, in hygienically safe edible products of high quality, and its medical applications.

However, this expansion in plastics application is being regarded to, an increasing extent with suspicion and criticism. There is a tendency by a large section of the public to have a preconceived negative attitude towards even well-proven plastics, which is being promoted and misused in certain areas. The statements in Table 1 are typical of the technically false statements made by some pressure groups.

Such objections to the use of plastics are propagated and supplemented further by novel and equally false arguments. They are presented partly with the intention of verifying biased views, with seemingly plausible arguments for acceptance by an uninformed public. This strategy follows the current trend — which should not be underestimated — of an increasing awareness of people with regard to their environment and health. Consequently, these objections and arguments are resonated in the media and by consumer groups, political parties, municipal bodies and, last but not least, among individual consumers. The success of this anti-plastics campaign is partly the result of inactivity during past decades by both plastics and additive producers as well as processors of the same. Thus, these bodies published only technical data and failed to inform the consumer in an understandable and objective fashion of the important properties of plastics, particularly with regard to aspects of environmental and consumer protection. Only after it became obvious that a major part of the public had been adversely influenced against plastics, did the industries concerned start to react with objective arguments. However, this attempt has been only partially successful. This is particularly obvious since numerous negative articles against plastics are still appearing in daily newspapers and journals. It is even more alarming that in some detailed expert judgements recently publicized by private and university institutes, the health and environmental hazards due to plastics have been assumed to be proven facts.[1,2]

Consequently, a number of concrete measures have been proposed, for instance, to substitute polyvinyl chloride (PVC) — a plastic that has very wide areas of application — to the maximum extent by other materials. This view is incomprehensible, particularly since PVC has a long-proven record of use in numerous fields of application throughout the world. In the Federal Republic of Germany, it has the second highest tonnage of polymeric material, exceeded only by polyolefins, of the order of 1.2 million tons per year. The easy modification of PVC through the use of additives, which have been evaluated positively over many years, represents a noteworthy technical asset. Table 2 shows the wide range of uses. It is not only used in the building and construction sector, but an increasing trend of its application also concerns the packaging of foodstuffs, as well as other consumer articles. In spite of this, PVC is now a permanent focal point of

Table 1. Technically false statements made by some pressure groups

1. The production and processing of plastics are wasteful with respect to resources and energy
2. Owing to the high volatility of starting materials and other ingredients, production and processing of plastics are hazardous for the health of factory workers
3. Plastic materials are dangerous for the environment and health, and, owing to their content of processing aids and other additives, they are potential sources of environmental pollutants
4. Society is faced with health hazards, among others, owing to the use of plastics in packaging and as building and construction materials, for example, through contamination of foods and beverages and of the air in rooms by volatile plastic components
5. Treatment and disposal of household and commercial wastes containing, in addition to vegetable components, glass, metals, paper and cardboard, and considerable quantities of different types of plastics, are problematic and hazardous.

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Table 2. Industrial application of PVC in different areas of usage in the Federal Republic of Germany

Industrial sector	Fraction (%)
Building and construction	58
Packagings	17
Automobiles	4
Electrical engineering	4
Furniture	4
Construction of apparatus and equipment	1–2
Consumer goods	3–6
Agriculture	1–2
Medicine	1–2
Mining	1–2

criticism, mainly in respect of its increasing application as a packaging material. The main objections are concerned with health hazards and problems concerned with disposal of PVC-containing household wastes. As far back as 1974, the American PVC producer B.F. Goodrich informed the 'Occupational Safety and Health Administration (OSHA)' that the death of several staff members due to liver angiosarcoma could possibly be related to vinyl chloride (VC) — the monomer of polyvinyl chloride (PVC). Thus, both VC and its polymer PVC came into the public attention for the first time. The resulting excitement was very intensive and quite often it was demanded that the use of VC, and consequently that of PVC, should be banned. Soon, thereafter, it was verified that VC is a cause of liver angiosarcoma. But it was also evident that, unlike its monomer, the polymer PVC was not toxic and could not be replaced easily on technical and economic grounds. Therefore, it became essential to remove hazards during the processing of VC, as well as reducing the level of residual VC in PVC to the lowest possible extent.

In retrospect, both as a result of protective regulations that came into effect from 1974 onwards, as well as action by PVC producers and processors, this problem was solved within a relatively short period. Thus, the methodical improvements of degassing VC polymerizates resulted in a reduction of residual VC to one thousandth of the amount contained in PVC materials produced by methods in vogue 15 years previously. The residual VC in processable PVC materials today is below about 1 mg VC per kg PVC (1 ppm) and is quite often below 0.1 mg VC per kg PVC (0.1 ppm).

After a short interruption, PVC has once again received a negative reaction from the media. This is not restricted to the environmental and health conscious German media but involves those of other western and northern European countries, the USA and Japan. The latest many sided objections to PVC are concerned mainly with its use in the packaging sector.

These are not only related to the production of PVC starting materials and the PVC produced, but also concern health hazards during the processing of PVC, the toxicity of PVC additives, risks to the consumer by the use of PVC as food and beverage packaging materials, and the disposal problems of used PVC packaging materials contained in household waste.

These arguments against PVC packaging materials have been raised on a broad front. However, they are only partially based on objective argument and verifiable facts. In most cases, the arguments have been selected with the sole objective of PVC substitution and they totally ignore, for instance, improved possibilities of energetic and/or material recycling of PVC wastes.

Moreover, the unique advantages of rigid PVC as food packaging material have not been considered at all. Two of the prime advantages can be cited as illustrations.

(i) As shown by results of numerous investigations[3–14] both aqueous and fat-releasing foodstuffs (including pure edible fats) come only into superficial contact with rigid PVC packaging materials and do not cause any appreciable swelling. Accordingly, in general, there is only a very limited possibility that mobile components of rigid PVC packaging material would migrate into the packed foodstuff. For example, the minimum and maximum total migrates, determined in cases of different polymeric packaging materials under identical and defined contact conditions, are compiled in Table 3.[15] The migration values are given in mg/dm^2 contact area between packaging material and fat-releasing foodstuff. The total migrate includes all components that migrate from a packaging material into a food product under defined contact conditions. It is clear that fat-releasing foodstuffs packed in

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Table 3. Total amount of components that migrate from different, plastic packaging materials into fat-releasing foodstuffs (test conditions: 10 days/40°C and one-sided contact between test specimen and test fat HB 307)

Plastic packaging material (polymer + additive)	Total migrate (mg/dm²)
Polyvinyl chloride (rigid PVC)	0[a]–2
Low-density polyethylene (LDPE)	4–14[b]
High-density polyethylene (HDPE)	2–9[b]
Polypropylene (PP)	2–7[b]
Impact-resistant polystyrene (HIPS)	1–6
Acrylonitrile butadiene styrene copolymerizate (ABS)	1–4

[a] Below detection limit.
[b] Dependent on thickness.

rigid PVC materials are less contaminated with migrating components than the other plastics. Consequently, the consumer has the lowest intake of contaminants from plastic packaging via food ingestion when rigid PVC materials are used exclusively for packaging. These observations are further substantiated by the values compiled in Table 4, which have been calculated from experimentally determined migration data and particular assumptions. These values refer to the daily additive intake by an individual consumer and are classified according to different additives of packaging materials.[15] Comparing the values in Table 4 shows that if, instead of polyolefins, rigid PVC is used exclusively for the packaging of foodstuffs, the consumer ingests about one-hundredth of the amount of plastic components (additives) as would be the case for polyolefins.

(ii) Within the framework of their numerous protective functions, packaging materials have to fulfil two important tasks. On the one hand, they must ensure that packed products reach the consumer without reduction of their characteristic quality, e.g. by retaining their original composition without loss of ingredients. On the other hand, they should protect against external influences that affect quality retaining properties. Thus, many foodstuffs, beverages and cosmetics have to be protected against loss of flavour, carbon dioxide or water. A particularly difficult packaging problem is that many products, particularly those containing fat, are sensitive to oxygen. On comparing (Table 5) the relative oxygen, carbon dioxide and water vapour permeabilities of a number of polymeric materials (relative to rigid PVC, which is presumed to have a permeability of 1 in each case), it is evident that rigid PVC, offers superior barrier characteristics. Thus, for instance, it is clearly indicated that,

Table 4. Daily uptake of migrated components of plastic packaging materials via food consumption; under the assumption that the foodstuffs are each only packaged in one of the listed packaging materials

Packaging material			Uptake of migrate by the consumer
Polymer	Additive	% by wt.	(mg/day)
HDPE	Antioxidant[a]	0.1	1.72
	BHT[b]	0.2	6.45
PP	Antioxidant[a]	0.1	
	BHT[b]	0.2	3.83
Rigid PVC	Stearyl Alcohol	0.6	0.006
	Stabilizer	1.0	0.02

[a] 3-(3,5-Di-*tert.*-butyl-4-hydroxyphenyl-*n*-octadecyl propionate.
[b] 2,6-Di-*tert.*-butyl-4-methylphenol.
[c] Di-*n*-oxtyltin-di-/mono-*n*-octyltin-tri (thioglycolic acid-2-ethyl-*n*-hexylester).

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Table 5. Relative permeabilities of different polymeric packaging materials, with respect to oxygen, carbon dioxide and water vapour (at 20 °C)

Packaging material (thermoplastic)	Gaseous/Vaporous component O_2	CO_2	H_2O
Polyvinylidene chloride (PVCD)	0.09	0.14	0.02
Acrylonitrile copolymer (PAN)	0.10	0.12	1.6
Polyvinyl chloride (PVC)	1.0	1.0	1.0
Polyethylene terephthalate (PETP)	1.2	0.8	1.2
6-Polyamide (PA)	1.5	4.3	5.3
Polypropylene (PP)	16	30	0.18
High-density polyethylene (HDPE)	20	39	0.09
Poystyrene (PS)	35	100	3.8
Low-density polyethylene (LDPE)	46	95	0.24

compared with various types of commonly used plastics, rigid PVC is most suitable for packaging O_2-sensitive and/or CO_2-containing products. Equivalent properties are only attained with composite plastic materials, produced by combining one of the other plastic materials with, for instance, a layer of PVDC (polyvinylidene chloride). The resulting laminates are more expensive compared with PVC films.

These few examples have shown that the discussions regarding substitution of polyvinyl chloride (PVC) in the packaging sector should be carried out with much more caution than has been done up to now. In order to prepare the ground for a more objective discussion of this presumed problem, in Part II a short introduction will be given about production, processing and application of PVC as well as about the structure and effects of the organotin stabilizers used. Moreover, the human and ecotoxicological aspects of PVC and its stabilizers will be discussed.

PART II — THE THERMOPLASTIC POLYVINYL CHLORIDE

Retrospective glance

It was observed in 1835 by Regnault that if vinyl chloride, contained in a glass vessel, is allowed to stand in sunlight, then a white powder is formed. Thereby, he discovered polyvinyl chloride, abbreviated as PVC. Not until 1877, however, was a detailed chemical study of the way in which the monomer combined to form the macromolecule (PVC), i.e. the polymerization mechanism of vinyl chloride, carried out by Baumann. The first PVC production began in 1912 and was terminated after the First World War. Subsequently, PVC was forgotten for a time and reappeared only after about 20 years, as a non-combustible substitute for celluloid. During this period, Wick found that the processing of PVC can be improved considerably by using particular additives as well as by using new technological steps. Moreover, he also discovered that the properties of finished PVC products could be influenced considerably by proper selection of processing conditions. As a result, numerous applications of PVC were established and, from 1935 onwards, industrial production of PVC was started.

Industrial production

Today, the thermoplastic PVC is one of the most frequently used polymeric materials. With the exception of polyethylene, PVC is the most significant type of plastic in use.

The current starting materials for the production of PVC and its copolymers are chlorine and ethylene. These are obtained from sodium chloride (NaCl) and crude petroleum. As Figure 1 indicates, according to production variation, either vinyl chloride ($CH_2{=}CHCl$) or vinylidene chloride ($CH_2{=}CCl_2$) is produced from the two starting materials.

The monomer VC is gaseous at room temperature and can be liquified under pressure. As a

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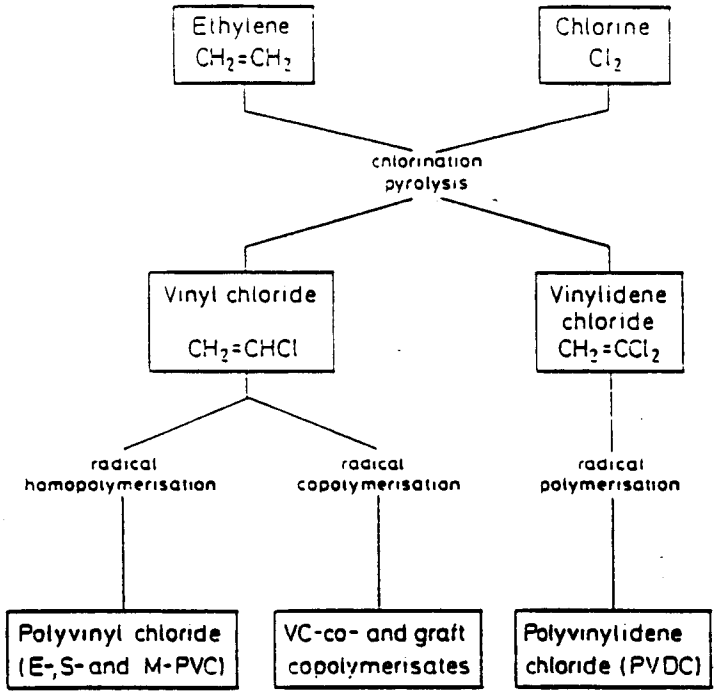

Figure 1. Processing diagram for production of polyvinyl chloride (PVC), VC-co- and graft, copolymerizates as well as polyvinylidene, chloride (PVDC)

result of its reactive double bond. VC can be converted easily to a radical by using an initiator (peroxides, etc.). As shown in Figure 2, this radical can add itself to another VC molecule, thus producing a dimeric VC radical. Finally, this reacts with further monomers to form long chains. The chain growth, the so-called polymerization, is interrupted by combination or disproportionation of two radicals. The length of a polymer chain depends to a considerable extent on the concentration of the initiator that starts radical formation as well as on the reaction conditions (temperature, time).

Industrial production of PVC is carried out by four different methods.

(i) *Emulsion polymerization (E-PVC).* In this, the oldest procedure, a system consisting of water, vinyl chloride (VC), emulsifier and water-soluble initiator is stirred in a pressure vessel (autoclave) at elevated temperature. Thereby, the less-water-soluble monomer VC is distributed as fine droplets, whereas the emulsifier forms the so-called 'miscella'. The vinyl chloride is confined within this miscella and the polymerization also takes place here. Then, as the confined VC is consumed, new VC diffuses into the miscella from free monomer droplets via the aqueous phase. This process continues until the entire vinyl chloride is polymerized. Thus, the miscella is gradually converted to solid polymer particles (latex particles). By means of nozzle spraying in a stream of hot air, the water is evaporated and the E-PVC is obtained as a powder.

(ii) *Suspension polymerization (S-PVC).* This procedure produces more than 80% of the PVC. The vinyl chloride monomer is distributed, as in the previous procedure, in an aqueous phase as droplets by using protective colloids. Contrary to the emulsion procedure, the polymerization in larger VC droplets is started by VC-soluble radical-forming agents and occurs in the organic phase. The PVC grains are separated from

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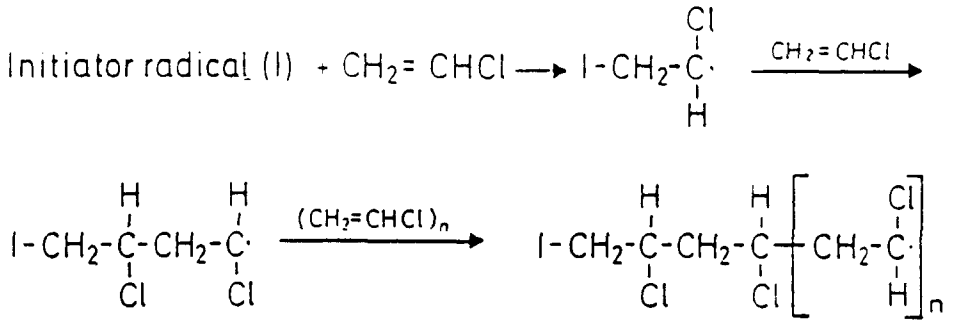

Figure 2. Radical homopolymerization of vinyl chloride (VC)

the aqueous phase by centrifuging and are then dried.

(iii) *Mass polymerization (M-PVC).* This procedure produces about 10% of PVC. The vinyl chloride monomer is directly polymerized in batches by using radical-forming agents. Since there is no requirement for the addition of water or other suspension agents, the drying step is omitted in this procedure, in contrast to the previously described emulsion and suspension polymerizations.

(iv) *Micro-suspension polymerization (Micro-S-PVC).* This procedure is similar, in principle, to the suspension polymerization described in (ii). However, in this case, a much finer droplet formation of vinyl chloride monomer in the aqueous phase is attained through special formulation and more intensive dispersion.

On the basis of these production methods, the current annual world production capacity of PVC amounts to 18 million tons. This is classified in Table 6 according to the different economic regions of the world.[16]

World-wide, about 15.5 million tons of PVC was processed in 1987. The production development in western Europe during past decades has been characterized by a steady increase until 1979, a drop in 1981 and then subsequent growth at a rate lower than that of other plastics (Figure 3).[16] The level of production in western and northern Europe during the 1980s amounted to an average of 80% installed capacity. This incomplete utilization of available production capacity resulted mainly from the concentration and restructuring processes in the western European PVC industry, leading to a reduction in the number of PVC producers in this region from 27 to 16 during 1981–1986.

Table 6. Production capacity (1987) of polyvinyl chloride (PVC) in different economic regions of the world

Economic region	Production capacity 10^6 (t/year)
North America	4.2
Western Europe (incl. Scandinavia)	5.1
Central and South America	1.1
Asia (excluding Japan and China)	1.7
Japan	2.6
Eastern Europe and China	3.0
Africa	0.3
Total	18.0

The production capacity of the seven PVC producers in the Federal Republic of Germany is around 1.4 million tons of PVC per year. After a drop during 1981–1982, the present utilization of capacity is again above 85%, which means an annual production of about 1.2 million tons PVC. Since 1983, the PVC consumption in the Federal Republic of Germany has again reached a level of more than 1 million tons per year. This corresponds to a per-head PVC consumption of nearly 18 kg per year.

Modification

In order to attain improved processing characteristics or special application profiles, polyvinyl chloride is either modified during the production process or is provided with additives before processing. This will be discussed elsewhere in more detail.

The first route mentioned offers the possibility of polymerizing vinyl chloride in the presence of

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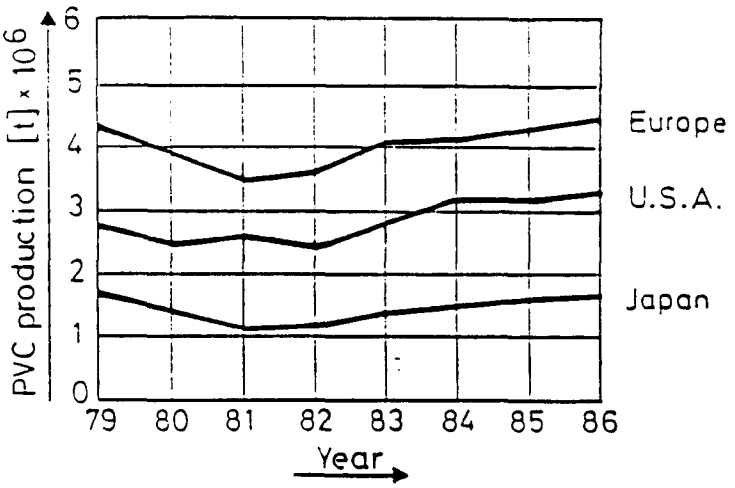

Figure 3. Trend of PVC production in western and northern Europe, USA and Japan during 1979–1986

other individual monomers (copolymerization) or to graft vinyl chloride onto other monomers that have already been pre-polymerized (graft polymerization). In this connection, more than 100 comonomers have been subjected to technical examination. As can be seen from the following list, only relatively few co- and/or graft polymerizates have been found to possess technical significance:

(i) vinyl chloride/vinyl acetate (and/or vinyl isobutyl ester) copolymerizates;
(ii) vinyl chloride/acrylic acid ester copolymerizates;
(iii) vinyl chloride/unsaturated dicarboxylic acid ester copolymerizates, e.g. copolymerization of VC with dibutyl maleic acid ester;
(iv) vinyl chloride/vinylidene chloride (VDC) copolymerizates (copolymerizates with 5–60% VDC content are processed to packaging films, specially used in laminates as a barrier layer against oxygen and water);
(v) vinyl chloride/olefine copolymerizates (copolymers consisting of VC and olefins, such as ethylene, propylene or isobutylene, possessing improved processing properties. In particular, VC/propylene copolymerizates containing 1–25% propylene increase thermostability, flowability and impact resistance. Since an inner plasticization of PVC occurs, low-molecular-weight plasticizers can be omitted);
(vi) graft copolymerizates of vinyl chloride, in combination with:
  (a) ethylene/vinyl acetate copolymerizates (EVA);
  (b) ethylene/propylene rubber (EPM(PEP));
  (c) ethylene/propylene/diolefin terpolymers (EPDM),
  (d) polyacrylic acid ester,
  (e) polyethylene, polybutadiene.

In addition, the PVC can be subjected to post-chlorination after polymerization, producing so-called 'chlorinated PVC (C/PVC)', which, instead of a normal chlorine content of 56.7% (homopolymeric composition), has a 62–69% chlorine content, giving it a higher thermal stability and lower flammability. Finally, it should also be mentioned that processable PVC can be mixed and/or blended with other polymers, e.g. chlorinated polyethylene, polyethylene copolymerizates, ABS and MBS polymerizates, resulting in the so-called polyblends.

Thus, by means of a specific modification of polyvinyl chloride, a number of disadvantageous characteristics of the polymer, e.g. low thermal stability, high melt viscosity, low flexibility, etc., can be compensated.

Processing

In the following, instead of describing different processing techniques, such as calendering and

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extrusion, blow and injection moulding, more attention will be given to the selection of crude PVC types and their furnishing with additives for making semi-finished goods, such as films, sheets and workpieces or finished products, such as cups, bowls and bottles.

According to type and intended use of the semi-finished or finished product, the optimum processing method is selected. Thereby, special demands are placed on the properties of PVC compounds used (the ready-to-use blend consists of PVC and suitable additives); for example, flowability and workability. These requirements can be met by proper selection of crude PVC, namely of emulsion, suspension or mass polymer, as well as by the addition of suitable processing aids (additives). In the course of selecting a particular type of crude PVC, in addition to the polymerization procedure, the K value — which is a measure of average degree of polymerization and of the related so-called internal viscosity — as well as the bulk density of the PVC are of particular significance. The different types of processing aids and other additives that are available for making processable PVC mixtures are shown in Figure 4. Stabilizers and lubricants are essential components. Accordingly, special PVC initial blends having differing contents of additives and varying K values are produced to meet the demands of the different processing conditions.

A review of the processing methods and the application of crude PVC types is given in Table 7.[17] Owing to the similarities of their characteristic profiles, it is difficult to make a qualitative differentiation between S-PVC and M-PVC. However, where special requirements are placed on the PVC finished product, for example, when high transparency is required, mainly M-PVC is used. On the other hand, only plasticized PVC mixtures from S-PVC are used for making cables, and Micro-S-PVC is preferentially used for paste processing. The most frequently used method for processing PVC compounds in the Federal Republic of Germany, with a share of 60%, is the extrusion moulding of pipes, films, profiles, etc. It is followed by calendering (films) with a share of 23% and by paste processing (synthetic leather, floor coverings, etc.) with a share of about 10%. Injection moulding, blowing of hollow bodies and compression moulding play a less significant role. These and other methods of processing PVC compounds are linked with the different temperature-dependent constitutional states of PVC. These are shown in Figure 5. The PVC materials cannot be deformed below the

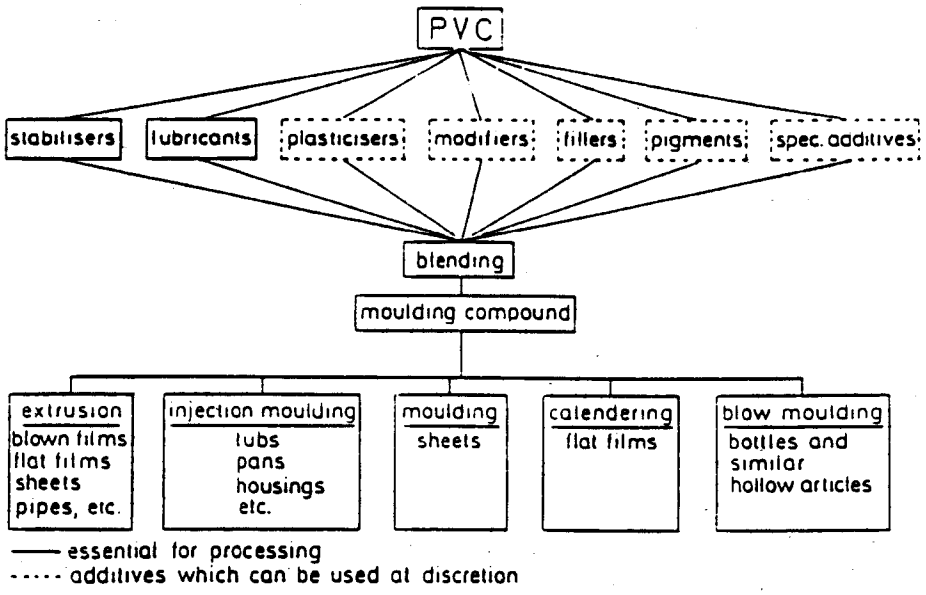

Figure 4. Preparation of PVC compounds for processing according to different methods

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Table 7. Use of PVC produced by different methods and their application in various types of product manufacture[a]

Manufacturing method	Type of PVC							
	S-PVC		M-PVC		Micro-S-PVC		E-PVC	
	Rigid	Plastic	Rigid	Plastic	Rigid	Plastic	Rigid	Plastic
Extrusion:								
pipes/hoses	++	++	++	+	–	–	+	–
window frames	++	–	–	–	–	–	–	–
cables	–	++	–	+	–	–	–	–
sheets/films	++	++	++	–	–	–	+	–
Blow moulding	+	–	++	–	–	–	–	–
Injection moulding	++	++	++	+	–	–	–	–
Calendering	++	++	+	+	–	–	++	+
Roll coating	+	++	+	+	–	–	–	–
Moulding	++	+	+	+	–	–	+	+
Spread coating/casting pastes	–	+	–	+	–	++	–	++
Powder sintering	++	+	–	+	–	–	++	–

[a]++, mainly; + lesser; – without significance.

glass transition temperature. Dependent on the type of PVC, this temperature is between 75 °C and 82 °C. Below this temperature, PVC products can be used in practice (application range) and can only be machine processed, e.g. by drilling, milling, sawing, etc.

Above the glass transition temperature, in the so-called softening range, the tearing tension of PVC increases steeply, reaching a maximum at about 95–100 °C in the thermo-elastic region. On further increase in temperature, it is again reduced (range II/III). These temperatures enable the formation of PVC products by, for example, deep-drawing, rolling or stretching.

If the temperature is increased even further, one exceeds range III of the so-called thermal

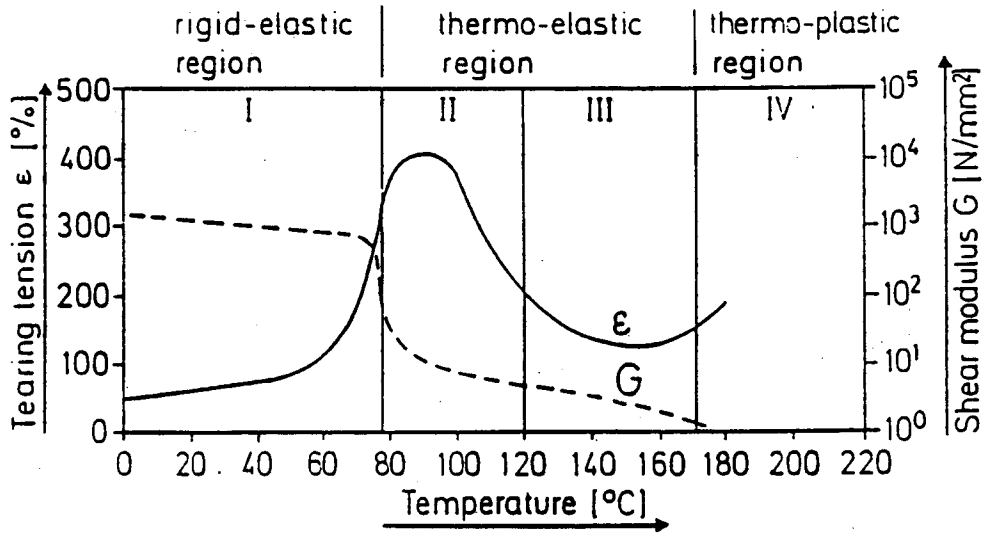

Figure 5. Individual states of PVC as well as the course of tearing tension and shear modulus as a function of temperature

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brittleness, reaching finally the melting range IV at 170°°C. The PVC melt is moulded by such processes as calendering, extruding, etc. in the so-called thermoplastic region between 170°C and 220°C, yielding products such as films, profiles, etc. that are resistant to deformation.

However, it should be noted that the thermal instability of pure PVC begins far below the melting temperature, namely from about 110°C upwards.[17,18] This thermolysis of PVC consists, to a major extent, of hydrogen chloride elimination in the technically interesting temperature region between 120°C and 220°C. This HCl elimination leads to polyene segments in the polymer and discoloration of the same from yellow to brown and finally black.[19] Simultaneously, the double bonds introduced into PVC are oxidized in the presence of oxygen to hydroxyl and carbonyl groups, and cracked in the last phase. This process leads to degradation of polymer chains and thus to a deterioration of the physical and chemical properties of PVC. Depolymerization reactions leading to vinyl chloride formation were not observed.

Generally, so-called thermal stabilizers have to be added to crude PVC. These additions prevent thermal degradation of the polymer during high-temperature processing. In addition to the thermostabilizing effect, these additives should possess the following properties and/or fulfil given requirements such as:

(i) optimum dispersion in PVC;
(ii) compatibility with all other components of the formulation;
(iii) low volatility and no plate-out tendency;
(vi) tasteless and odourless with respect to food packaging materials;
(v) physiologically harmless with respect to packaging materials and other articles according to legislative requirements (e.g. low tendency towards migration into packaged product);
(vi) low ecotoxicological potential;
(vii) light-stabilization of PVC products;
(viii) producing crystal-clear PVC for transparent packs or wrappers;
(ix) permanent maintenance of physical, chemical and electrical properties of finished PVC products.

Table 8. The most important groups of thermo- and light stabilizers and their consumption figures in western Europe during 1987

Stabilizer groups	Stabilizer consumption (10^3 t)	(%)
Lead compounds Oxides, sulphates, phosphites and carboxylates	49.0	56.0
Metal soaps Zn, Ca/Zn, Ba/Zn, Ba/Cd, Ba/Cd/Zn carboxylates (stearates, octoates, etc.)	28.5	31.9
Organic tin compounds Mono-*n*-octyltin-tris-/di-*n*-octyltin bis (2-ethyl-*n*-hexyl-thioglycolate)	9.5	11.0
Monomethyltin-tris-/dimethyltin bis (2-ethyl-*n*-hexyl-thioglycolate)		
Organic compounds, free from metals Aminocrotonic acid ester (with alcohols $\geq C^{12}$) Diphenylthiourea 2-phenyl indole	0.5	0.5
Total	87.5	99.4

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No known stabilizer possesses by itself all these characteristics to the extent required for processing and application in practice. Consequently, optimum stabilizers have to be selected according to different processing procedures and application areas. In fact, quite often synergetic mixtures of several stabilizers are used.

The four most important groups of thermo- and light stabilizers, including several characteristic representatives, as well as their consumption figures in western Europe, are given in Table 8.[20,21]

The use of lead- and cadmium-containing stabilizers are facing increasing opposition owing to their presumed human and ecotoxicological effects. This ignores the fact that stabilizer systems containing heavy metals contribute towards excellent thermo- and light stability of PVC and that the stabilized PVC is not used for packaging foodstuffs, medicines, etc. Despite this, attention is drawn to the fact that although cadmium-containing systems are relatively small compared with lead-containing stabilizers, in the Federal Republic of Germany alone about 450 t of Cd are used annually in the form of PVC stabilizers. If the quantity of cadmium-containing pigments in PVC is ignored, the above amount of Cd corresponds to about 25% of the total cadmium consumption in the Federal Republic of Germany.

However, in view of the quite considerable quantity of heavy metals used and the fact that cadmium can enter the human body via aquatic, air and soil-plant routes, the Cd-containing soaps, used nowadays only for stabilization of durable rigid PVC items such as window profiles, shutters and facade elements, are classified as being objectionable. This has been recognized by the plastics processing industry, which is making every effort to substitute the Cd-as well as Pb-containing stabilizers with Ba–Sn and/or Ca/Sn compounds.

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