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1. Introduction

1.1. Definition

A plasticizer is a substance incorporated into a material to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the product. Plasticizers are inert, organic substances with low vapor pressures, predominantly esters, which react physically with high polymers to form a homogeneous physical unit, whether it be by means of swelling or dissolving or any other [1].

At present some 300 plasticizers are manufactured, of which at least 100 are of commercial

importance. A list of some of the most widely used plasticizers is given in Table 1.

1.2. Types of Plasticization

Two principle ways of obtaining the plasticization effects described above are commonly utilized. Firstly, a rigid polymer may be *internally plasticized* by chemically modifying the polymer or the monomer so that the flexibility of the polymer is increased. A rigid polymer, however, can also be *externally plasticized* by addition of a plasticizer, which imparts the desired flexibility but is not chemically changed by reaction with the polymer. The latter process has

Table 1. Plasticizers in Common Use

Plasticizer	Abbreviation	Alcohol carbon number	CAS registry no.	M_r	Density at 20 °C, g/cm ³
Phthalates					
Diisobutyl phthalate	DIBP	4	[84-69-5]	278.3	1.039
Dibutyl phthalate	DBP	4	[84-74-2]	278.3	1.046
Diisooheptyl phthalate	DIHP	7	[41451-28-9]	362	0.991
L79 phthalate	L79P, 79P	7 – 9	[71888-89-6]	380	0.985
L711 phthalate	L711P, 711P	7 – 11	[68648-91-9]		0.971
Diocetyl phthalate	DOP	8	[117-81-7]	390	0.984
Diisooctyl phthalate	DIOP	8	[27554-26-3]	390	0.983
Dinonyl phthalate	DNP	9	[84-76-4]	419	0.97
Diisononyl phthalate	DINP	9	[28553-12-0] [68515-48-0]	419	0.975
Diisodecyl phthalate	DIDP	10	[68515-49-1]	447	0.967
L911 phthalate	L911P, 911P	9 – 11	[68515-43-5]	454	0.96
Diundecyl phthalate	DUP	11	[3648-20-2]	474	0.953
Diisoundecyl phthalate	DIUP	11	[85507-79-5]	474	0.962
Undecyl dodecyl phthalate	UDP	11 – 12	[68515-43-5]	488	0.957
Diisotridecyl phthalate	DTDP	13	[27253-26-5]	531	0.952
Butyl benzyl phthalate	BBP	4 – 7	[68515-47-9]	312.3	1.119
Adipates					
Diocetyl adipate	DOA	8	[103-23-1]	370.6	0.929
Diisononyl adipate	DINA	9	[33703-08-1]	398	0.929
Diisodecyl adipate	DIDA	10	[27178-16-1]	427.1	0.915
Trimellitates					
Triocetyl trimellitate	TOTM	8	[3319-31-1]	530	0.991
L79 trimellitate	L79TM	7 – 9	[68515-60-6]	530	0.996
L810 trimellitate	L810TM	8 – 10	[67989-23-5]	592	0.973
Phosphate esters					
Tri-2-ethylhexyl phosphate	TOF	8	[78-42-2]	434	0.926
2-Ethylhexyl diphenyl phosphate	Santicizer 141	6 and 8	[1241-94-7]	362.4	1.091
Tricresyl phosphate	TCP	6	[1330-78-5]	368.2	1.165

the advantage of lower cost and permits the fabricator freedom in devising formulations to manufacture items of differing flexibility simply by adding different amounts of plasticizer, within the constraints of polymer – plasticizer compatibility.

1.3. Types of Plasticizer

Plasticizers can be divided into two principal groups: primary and secondary. *Primary plasticizers* lower the glass transition temperature T_g and increase the elongation and softness of the polymer. *Secondary plasticizers*, when added to the polymer alone, do not bring about such changes and may also have limited compatibility with the polymer. However, when added to the polymer in the presence of a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer.

2. Plasticizers in Common Use

2.1. Market Overview

The list of commercially available plasticizers, covering applications throughout polymer science, is extensive. This reflects the development of plasticizers to meet the increasing demand for polymers, especially PVC, for new and higher quality applications. This article discusses the main groups of plasticizers; for further details, see [1–4] and references therein.

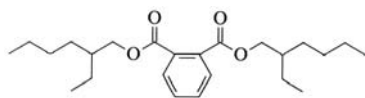
The Western European plasticizer market had a capacity of 969×10^3 t/a in 1989 and at that time was growing at a rate of 3 % per annum [5]. In 1996 production of plasticizer in Western Europe amounted to 1253×10^3 t/a and in the United States to 636×10^3 t/a [6]. In terms of plasticizer types, the majority of this tonnage (>85 %) is standard phthalate (esters of phthalic anhydride with C₈ – C₁₀ alcohols). Reasons for this are the

relatively low price and ready availability of feedstocks. The remainder of the market is taken up by phthalate esters of other alcohols, specialty phthalates, adipates, trimellitates, and other esters.

2.2. Phthalate Esters (see also → Phthalic Acid and Derivatives)

Diesters of phthalic anhydride are produced commercially from $C_1 - C_{13}$ alcohols, although the $C_1 - C_3$ esters are generally too volatile to find widespread use. Di-*n*-butyl phthalate (DBP) and diisobutyl phthalate (DIBP) (linear and branched C_4 esters) are used in many PVC formulations, principally for ease of gelation. Owing to their relatively high volatility, in comparison with other phthalates, they are often used in conjunction with higher molecular mass esters. Diisopentyl phthalate (DIPP) is generally used in a similar manner. Diisooheptyl phthalate (DIHP), an ester based on a C_7 iso-alcohol from the oxo alcohol process, shows good plasticizing action with PVC as well as with a number of other polymers [4]. Its principle use in PVC, when compared with higher molecular mass plasticizers, lies in its gelation characteristics and balance of volatility and viscosity, the volatility of DIHP being only slightly higher than the corresponding C_8 phthalate (DIOP).

Di-2-ethylhexyl phthalate (DEHP) (also known as dioctyl phthalate, DOP) has long been accepted as the industry standard general purpose primary plasticizer.



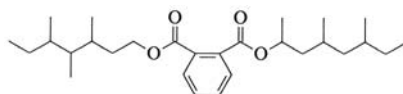
Di-2-ethylhexyl phthalate, DEHP
(dioctyl phthalate, DOP)

This is because its properties are adequate for many applications in the flexible vinyl industry. DEHP shows good gelation characteristics, good softening action, and adequate viscosity properties in emulsion PVC pastes. Diisooctyl phthalate, produced from C_8 oxo alcohols, shows performance in PVC which is generally similar to DEHP. Di-*n*-octyl phthalate (DnOP), a C_8 phthalate ester derived from a linear alcohol, is also produced, but in far smaller quantities than

the branched phthalates. The linear structure imparts improved low-temperature performance and lower viscosity.

Diisononyl phthalate (DINP) is produced from C_9 oxo alcohols and has similar plasticizing properties to DEHP. Its slightly higher molecular mass results in a somewhat lower plasticizer efficiency which requires a greater addition of plasticizer to impart an equivalent softness (these effects are discussed in detail in Section 4.2.1). The higher molecular mass alcohol also imparts improved high-temperature performance and resistance to extraction. Other C_9 phthalates are also produced [e.g., DNP, DINP(S)] and vary in the linearity of the alcohol component in the ester, the more linear varieties giving improved properties.

Diisodecyl phthalate (DIDP), the phthalate ester of C_{10} oxo alcohols, exhibits superior high-temperature performance to DINP and DEHP due to its higher molecular mass (lower volatility).



Diisodecyl phthalate, DIDP
(one of the possible isomers)

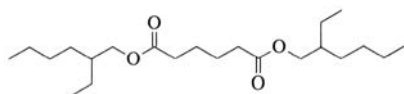
Its lower plasticizing efficiency compared to the lower phthalates requires greater plasticizer addition to impart the same softness, although this can, in some cases, be advantageous. Diundecyl phthalate (DUP), diisoundecyl phthalate (DIUP) and undecyl dodecyl phthalate (UDP) continue this trend. Ditridecyl phthalate (DTDP) is the highest molecular mass phthalate ester generally available in commercial quantities. Its high molecular mass results in low plasticizing efficiency, and some compatibility problems may occur at high plasticizer loadings. Its low volatility, however, also results in superior high-temperature performance and allows some strict electrical cable insulation and sheathing specifications to be met.

2.3. Adipate Esters

Alkyl esters of adipic acid have two principle advantages in the plasticization of PVC resins in comparison with the corresponding phthalate ester: (1) their lower intrinsic viscosity confers

lower plastisol viscosity and good plastisol storage stability, enabling use in demanding applications and (2) they give superior low-temperature flexibility properties.

Of adipate esters in use in the flexible vinyl industry, di-2-ethylhexyl adipate, DEHA (also known as dioctyl adipate, DOA) is the most common.

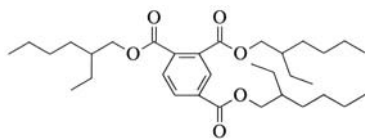


Di-2-ethyl hexyl adipate, DEHA
(dioctyl adipate, DOA)

It is widely used in flexible PVC food film (cling film). DEHA has good plasticizing efficiency and compatibility with PVC, and its very low viscosity enables it to be used in PVC plastisol applications where low viscosity is required, often in conjunction with a phthalate. Diisononyl adipate (DINA) is the ester of adipic acid with isononanol produced from oxo alcohols. It shows similar properties to DEHA. Its higher molecular mass does, however, increase its viscosity compared with DEHA, but this is accompanied by a reduction in volatility. The lower efficiency in comparison with DEHA, which requires a greater plasticizer addition, can result in lower plastisol viscosities. These effects are extended in moving to diisodecyl adipate (DIDA). Higher adipates (e.g., ditridecyl adipate, DTDA) are of limited use due to their lower compatibility with PVC.

2.4. Trimellitate Esters

Esters of trimellitic anhydride (TMA) have grown in popularity due to their excellent thermal properties and resistance to extraction. Tris-2-ethylhexyl trimellitate (TOTM), produced from trimellitic anhydride and 2-ethylhexanol, is the ester most widely used.

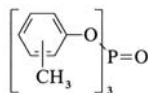


Tris-2-ethylhexyl trimellitate
(trioctyl trimellitate, TOTM)

Although of a lower plasticizing efficiency than the corresponding phthalate, the thermal stability and extraction resistance of TOTM are superior. These properties can be improved still further by using trimellitate esters produced from mixed linear alcohols, e.g., L79 trimellitate and L810 trimellitate. The improved properties brought about by these esters are discussed further in Chapter 4.

2.5. Phosphate Esters

The principle advantages of phosphate esters such as tricresyl phosphate as plasticizers for PVC is their low volatility and their ability to impart fire-retardant properties to a PVC formulation.



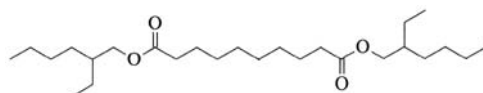
Tricresyl phosphate

Tris(2-ethylhexyl) phosphate shows good compatibility with PVC and also imparts good low-temperature performance in addition to good fire retardancy.

2-Ethylhexyl diphenyl phosphate has wide-spread use due to its combination of plasticizing efficiency, low-temperature properties, migration resistance, and fire retardancy.

2.6. Sebacate and Azelate Esters

Esters from the linear sebacic and azelatic acids are used in PVC applications for the same reasons as the corresponding adipates, i.e., low viscosity and good low-temperature performance. Di-2-ethylhexyl sebacate (DOS) and di-2-ethylhexyl azelate (DOZ) are the most widely used.

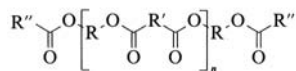
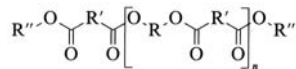


Di-2-ethylhexyl sebacate, DOS

In comparison to adipates, however, these esters tend to have a significantly higher cost and consequently only find use in extreme low-temperature applications.

2.7. Polyester Plasticizers

Polyester plasticizers, or polymeric plasticizers as they are more generally known, have found use due to their low volatility and high extraction resistance.



Polymeric plasticisers

They are typically based on condensation products of propane- or butanediols with adipic acid or phthalic anhydride. The growing polymer chain may then be end-capped with an alcohol or a monobasic acid, although non-end-capped polyesters can be produced by strict control of the reaction stoichiometry. Due to their higher molecular mass compared to other plasticizers they have much higher viscosities (3 – 10 Pa · s), which in some cases can make processing with PVC difficult.

2.8. Sulfonate Esters

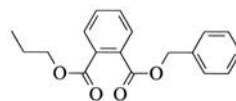
Sulfonate ester plasticizers for PVC are typically aryl esters of a C₁₃ – C₁₅ alkane sulfonic acid. They are relatively efficient and easily processable plasticizers with good extraction properties.

2.9. Specialty Phthalate Esters

In addition to the phthalate plasticizers described in Section 2.2, other phthalate plasticizers are also commercially available. These are speciality products which find use as high-quality plasticizers in specific applications. Their quality tends to be reflected in their price since they require either a further manufacturing stage (e.g., transesterification) or the use of alcohol feedstocks of greater linearity than the standard phthalates.

Benzyl butyl phthalate (BBP) shows excellent compatibility and fusion characteristics with PVC and is widely used in vinyl flooring for

these reasons and also due to its superior stain resistance.



Benzyl butyl phthalate, BBP

Linear and semilinear phthalates (e.g., DnOP, 911P, DUP) have lower viscosities than the corresponding branched ester. This results in lower plastisol viscosity and also lower plasticizer volatility. 911P, a phthalate ester based on linear and semilinear C₉ – C₁₁ alcohols, is the premium plasticizer for flexible PVC in automotive applications due to its low fogging (the condensation of volatile material on a car windscreen, causing impaired visibility); see Section 4.2.7.

2.10. Secondary Plasticizers

Secondary plasticizers (also referred to as extenders) continue to play a major role in flexible PVC technology. They do not have the same mode of softening action as a primary plasticizer but do impart softening behavior when used in combination with a primary plasticizer. In some very hard PVC formulations, however, a secondary plasticizer alone may be of use. The major secondary plasticizers are chlorinated hydrocarbons. These are hydrocarbons chlorinated to varying amounts, typically 30 – 70%. For a given hydrocarbon, plasticizer viscosity increases with increasing chlorine content. Chlorinated hydrocarbons of the same chlorine content may, however, have different volatilities and viscosities if they are based on different hydrocarbons. The principal advantages of such materials are: (1) they improve fire retardancy due to their chlorine content and (2) formulations containing a secondary plasticizer are often cheaper. Precise knowledge of compatibility between standard plasticizers and chlorinated paraffins is required since some mixtures become incompatible with each other and the PVC resins at certain concentrations. Phthalate – chlorinated hydrocarbon compatibility decreases as the molecular mass of the phthalate and the plasticizer loading in the PVC increases; for specific examples, see [1].

3. Mechanism of Plasticizer Action

Several theories of plasticizer action have been proposed, ranging in detail and complexity. Whilst each theory is not exhaustive, an understanding of the plasticization process can be gained by combining ideas from each theory. The theories are discussed in detail in [1].

3.1. The Lubricity Theory

The lubricity theory is based on the assumption that the rigidity of the resin arises from intermolecular friction binding the chains together in a rigid network. On heating, these frictional forces are weakened so as to allow the plasticizer molecules between the chains. In the resulting mixture at room temperature the plasticizer molecules act as lubricants for the polymer chains.

3.2. The Gel Theory

The gel theory extends the lubricity theory in that it deals with the idea of the plasticizer acting by breaking the resin – resin attachments and interactions and by masking these centers of attachment from each other, preventing their reformation. Such a process may be regarded as being necessary but by itself insufficient to explain a completely plasticized system since while a certain concentration of plasticizer molecules will provide plasticization by this process the remainder will act more in accordance with the lubricity theory, with unattached plasticizer molecules swelling the gel and facilitating the movement of plasticizer molecules, thus imparting flexibility. Molecules acting by this latter action may in fact constitute the bulk of plasticizer molecules.

3.3. The Free-Volume Theory

The free-volume theory extends the above ideas and also allows a quantitative assessment of the plasticization process. The free volume of a polymer is described by Equation 1 and Figure 1

$$V_f = V_t - V^0 \quad (1)$$

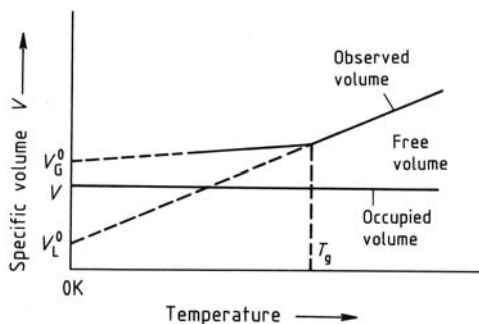


Figure 1. The free-volume concept [4]

where

V_f = the free volume of the polymer

V_t = specific volume at temperature t

V^0 = specific volume at arbitrary reference point, usually 0K

and V_G^0 and V_L^0 are the specific volumes of the glass and liquid extrapolated to 0K.

Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. Figure 1 shows how the amount of free volume in the polymer increases sharply at the glass transition temperature T_g . Consequently, the study of plasticization is a study of how to lower T_g , thus creating a polymer that is flexible at ambient temperature. Plasticizers therefore increase the free volume of the resin and also ensure that free volume is maintained as the resin – plasticizer mixture is cooled from the melt. Combining these ideas with the gel and lubricity theories implies that plasticizer molecules that do not interact with the polymer chain must simply fill free volume created by those molecules that do. These molecules may also be envisaged as providing a screening effect that prevents interactions between neighboring polymer chains, thus preventing reformation of the rigid polymer network on cooling.

For the plasticized resin, free volume can arise from:

1. Motion of the chain ends
2. Motion of the side chains
3. Motion of the main chain

These motions can be increased in a variety of ways, including:

1. Increasing the number of end groups
2. Increasing the length of the side chains
3. Increasing the possibility of main chain movement by the inclusion of segments of low steric hindrance and low intermolecular attraction
4. Introduction of a lower molecular mass compound which imparts the above properties
5. Raising the temperature

The introduction of a plasticizer, which has a lower molecular mass than the resin, can impart a greater free volume per volume of material since (1) there is an increase in the proportion of end groups and (2) it has a lower glass transition temperature T_g than the resin. A detailed mathematical treatment of this [7] can be carried out to explain the success of some plasticizers and the failure of others. Clearly, the use of a given plasticizer in a certain application will be a compromise between the above ideas and physical properties such as volatility, compatibility, high- and low-temperature performance, and viscosity. This choice will be application dependent, i.e., there is no ideal plasticizer for every application.

3.4. Solvation – Desolvation Equilibrium

Since plasticizer migrates from plasticized polymers, it is clear that plasticizer molecules are not bound permanently to the polymer as in an internally plasticized resin, but that an exchange or equilibrium mechanism is present. This implies that there is no stoichiometric relationship between polymer and plasticizer, although some quasistoichiometric relationships appear to exist [8], [9]. This idea is extended in Section 3.6.

3.5. Generalized Structure Theories

In their simplest form generalized structure theories attempt to produce a visual representation of the mechanism of plasticizer action [1]. The theories are based on the concept that if a small amount of plasticizer is incorporated into the polymer mass it imparts slightly more free volume and gives more opportunity for the movement of macromolecules. Many resins tend to become more ordered and compact as existing

crystallites grow or new crystallites form at the expense of the more fluid amorphous material. For small additions of plasticizer, the plasticizer molecules may be totally immobilised by attachment to the resin by various forces. These tend to restrict the freedom of motion of small portions of the polymer molecule necessary for the absorption of mechanical energy. Therefore it results in a more rigid resin with a higher tensile strength and modulus than the base polymer itself. This phenomenon is therefore termed anti-plasticization. A study by HORSLEY [10] used X-ray diffraction to show that small amounts of dioctyl phthalate (DOP) progressively increase the order in the PVC. Above these concentrations the order decreases and the polymer becomes plasticized (see also Section 3.6).

3.6. Specific Interactions and Interaction Parameters

Early attempts to describe PVC – plasticizer compatibility were based on the same principles as used to describe solvation, i.e., “like dissolves like” [11]. To obtain a quantitative measure of PVC – plasticizer compatibility a number of different parameters have been used. These are briefly described below.

The Hildebrand Solubility Parameter δ gives a measure of compatibility between plasticizer and a resin based on the solvating power of the plasticizer for the resin under investigation. For complex molecules this can be estimated [12] by using a set of additive constants for the more common groups in plasticizer molecules. These constants are designated F and the overall value for the plasticizer is given by the equation

$$\delta = \sum F/V \quad (2)$$

i.e., a summation of each solubility constant for each molecular portion of the plasticizer molecule divided by the molecular volume. Data so calculated for different plasticizers can be compared, with the higher values suggesting greater compatibility.

The Polarity Parameters Φ were evaluated by VAN VEERSEN and MEULENBERG [13] and despite their apparent simplicity they show a good

correlation with plasticizer activity for nonpolymeric plasticizers. The parameter is defined as:

$$\Phi = \frac{M(A_p/P_o)}{1000} \quad (3)$$

where

M = molecular mass of plasticizer

A_p = number of carbon atoms in the plasticizer, excluding aromatic and carboxylic acid carbon atoms

P_o = number of polar (e.g., carbonyl) groups present

The factor of 1000 is used to produce values of a convenient size.

The Solid-Gel Transition Temperature

T_m is a measure of plasticizer activity. It is the temperature at which a single grain of PVC dissolves in excess plasticizer. More efficient plasticizers have lower values of T_m due to their higher solvating power.

The Flory – Huggins Interaction Parameter χ . These ideas, based on a study of polymer miscibility, were applied to plasticizers by ANAGNOSTOPOULOS [14] according to the equation:

$$1/T_m = 0.002226 + 0.1351(1-\chi)/V_1 \quad (4)$$

where V_1 is the molar volume of the plasticizer, calculated from the molecular mass and the density at T_m .

The Activity Parameter α . is based on work by BIGG [15]. It is another measure of plasticizer activity and is defined as

$$\alpha = 1000 \frac{(1-\chi)}{M} \quad (5)$$

Summaries. Over the past few years these methods have been assessed and extended by many workers, in particular the Loughborough group [16], [17]. It was shown that solubility parameters are capable of classifying plasticizers of a given family in terms of their compatibility with PVC but that they are of limited use for comparing plasticizers of different families (e.g., phthalates with adipates). Polarity parameters provided useful predictions of the activity of monomeric plasticizers but again were not able

to compare activity of plasticizers from different families. In all cases it was not possible to predict the behavior of polymeric plasticizers.

Specific Interactions. Ideas on the subject of specific interactions between PVC and a plasticizer molecule, as a basis of plasticization, can be considered a more detailed form of some of the ideas discussed above. Clearly some mechanism of attraction and interaction between PVC and plasticizer must exist for plasticizer to be retained in the polymer after processing.

The role of specific interactions in the plasticization of PVC has been proposed from work on specific interactions of esters in solvents (e.g., hydrogenated chlorocarbons) [18], work on blends of polyesters with PVC [19–25], and work on plasticized PVC itself [26–28]. Modes of interaction between the carbonyl functionality of the plasticizer ester or polyester were proposed, mostly on the basis of results from Fourier transform IR spectroscopy (FTIR). Shifts in the absorption frequency of the carbonyl group of the plasticizer ester to lower wavenumber, indicative of a reduction in polarity (i.e., some interaction between this functionality and the polymer) were reported [25–27]. Work performed with dibutyl phthalate [27] suggested an optimum concentration at which such interactions were maximized. Spectral shifts were in the range $3 - 8 \text{ cm}^{-1}$. Similar shifts were also reported in blends of PVC with polyesters [19–25], again showing a concentration dependence of the shift to lower wavenumber of the ester carbonyl absorption frequency.

Recent Studies. Some recent work has extended these ideas by using new analytical techniques, in particular molecular modeling and solid-state NMR spectroscopy.

Molecular Modeling. The computer modeling of molecules is a rapidly growing branch of chemistry (\rightarrow Molecular Modeling) [29–31]. High-resolution graphics and fast computers allow the operator to build molecules in minimum energy configurations and view them in real time. This model can be constructed from crystallographic coordinates available from data bases or by simple intervention from the operator. Molecular mechanics or quantum mechanics programs are then used to arrive at a likely structure.

A range of plasticizer molecule models and a model for PVC were generated and energy minimized to observe their most stable conformations. Such models highlighted the free volume increase caused by the mobility of the plasticizer alkyl chains. More detailed models were also produced to concentrate on the polar region of the plasticizer and its possible mode of interaction with the polymer. These showed the expected repulsion between areas on the polymer and plasticizer of like charge as well as attraction between the negatively charged portions of the plasticizer and positively charged portions of the PVC.

Solid-State NMR Spectroscopy. Recent advances in technology have made the study of solids by NMR techniques of considerably greater ease than in previous years. For the accumulation of solid state ^{13}C NMR spectra, cross polarisation magic angle spinning (CP-MAS) can be utilized to significantly reduce signal broadening effects present in the solid state but not in the liquid state. The technique was used to study the molecular effects of plasticization by comparing spectral shifts of PVC and plasticizer under various degrees of processing. For PVC plasticized with DIDP two processing temperatures, 130 °C and 170 °C, were used, representing a low degree and high degree of plasticization, respectively. The comparison of the spectra showed no shift in the resonance frequency of the carbonyl group with processing temperature. The most significant difference in the two spectra was in the aliphatic carbon resonances. The spectra of the more plasticized sample showed resonance shifts and increased resolution for these carbon atoms. This again shows a strong dependence of successful plasticization on the conformation of the alkyl chains of the plasticizer ester (linked to the increased free volume).

4. Plasticized PVC

4.1. Applications Technology

Over 90 % of plasticizer sales by volume are into the PVC industry. The reason is that the benefits imparted by the plasticization of PVC are far greater than those imparted to other polymers. PVC stands alone among polymers in its ability

both to accept and retain large concentrations of plasticizer. This is due to a morphological form consisting of highly amorphous, semicrystalline, and highly crystalline regions. Without the wide range of additives available (e.g., plasticizers, stabilizers, fillers, lubricants, pigments) PVC would be of little use. The development of PVC as a commodity polymer is fundamentally linked to the development of its additives.

The two principle types of PVC are suspension and emulsion PVC. The plasticizer applications technology associated with these two forms are different and are discussed separately here. Details of the polymerization techniques giving rise to these two distinct polymer types are discussed in [2], [32]; (see also → Poly(Vinyl Chloride)).

4.1.1. Suspension PVC

PVCs produced by suspension polymerization have a relatively large particle size (typically 100 – 150 μm). Additionally, these particles are highly porous and are therefore able to absorb large amounts of liquid plasticizer during a formulation mixing cycle. Flexible PVC formulations based on a suspension polymer are typically processed by a dry-blend process, during which all formulation ingredients are heated (typically 70 – 110 °C) and intimately mixed to form a dry powder (PVC dry-blend) which contains all formulation ingredients. This dry-blend can be either stored or processed immediately. Processing of suspension resin formulations is performed by a variety of techniques such as extrusion, injection molding, and calendaring to totally fuse the formulation ingredients and form the desired product.

4.1.2. Emulsion PVC

Emulsion PVC resins differ from those manufactured by the suspension process principally in terms of particle size but also in the presence of emulsifiers and surfactants not used in suspension polymerization. The particle size of an emulsion polymer (typically 1 – 2 μm) is much lower than that of a suspension resin. This low particle size imparts a lack of porosity to the resin and thus the mixing of formulation ingredients in

a dry-blending process is not possible. A typical flexible PVC formulation prepared with an emulsion polymer will be a liquid or paste (plastisol). This consequently leads to a different applications technology area. PVC plastisols can be fused by techniques such as spreading, rotational molding, and slush molding. Plastisols may also be semi-gelled (i.e., enough heat is imparted to convert the plastisol into a solid but without the full development of tensile properties brought about by complete fusion) for storage.

As the formulation ingredients in a plastisol are in the liquid form, the viscosity of the plastisol is of major importance, and the intrinsic viscosity of the plasticizer has a major contribution to the plastisol viscosity, as do the polymerization conditions of the resin. The desired plastisol viscosity can be obtained by careful selection of polymer, plasticizer, and other formulation ingredients but also by shear rate. PVC plastisols are either (1) pseudoplastic or shear-thinning (viscosity decreases with shear), (2) near-Newtonian (viscosity remains nearly constant with shear), or (3) dilatant (viscosity increases with shear). Choice of plastisol ingredients to give desired viscosity effects will depend on the application requirements of the plastisol.

4.2. Effect of Plasticizer Choice on the Properties of Flexible PVC

This section discusses the effect of plasticizer choice on a range of properties of flexible PVC articles. Certain properties are more important for some applications than others, and hence some plasticizers find more extensive use in some application areas than others. The PVC technologist must ascertain the most important properties for the application in question and then make the correct choice of plasticizer.

4.2.1. Plasticizer Efficiency

Plasticizer efficiency is a measure of the concentration of plasticizer required to impart a specified softness to PVC. The softness may be measured as a British Standard Softness (BSS) or a Shore hardness (BSS 35 is equivalent to a Shore A hardness of 80—test method BS 2782). For a given acid constituent of plasticizer ester, plasti-

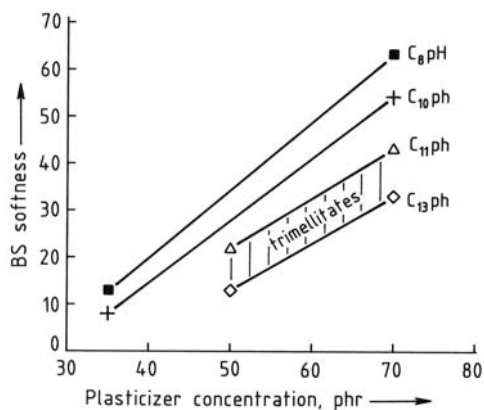


Figure 2. Relative efficiency of plasticizers
ph = phthalate

cizer efficiency decreases as the carbon number of the alcohol chain increases; e.g., for phthalate esters efficiency decreases in the order DBP > DIHP > DOP > DINP > DIDP > DTDP. For example, an additional six parts per hundred of PVC (phr) of DIDP than DOP is required to give a hardness of Shore 80 when all other formulation ingredients remain constant. In addition to the size of the alcohol chain, the amount of branching is also significant, with the more linear isomers being of greater efficiency. Choice of the acid constituent can also be significant. For the same alcohol constituent, phthalate and adipate esters are approximately equivalent but both are considerably more efficient than the corresponding trimellitate.

Figure 2 compares various plasticizers with respect to their ability to impart flexibility to a PVC resin. This shows the lower plasticizing efficiency of a C₁₀ phthalate relative to a C₈ phthalate and also the lower plasticizing efficiency of the trimellitate esters compared to the phthalates.

4.2.2. High-Temperature Performance

High-temperature performance in flexible PVC is related to (1) plasticizer volatilization and (2) plasticizer degradation. Plasticizer volatilization, both from the finished article during use at elevated temperatures (e.g., electrical cable insulation) and also during processing (i.e., release of plasticizer fume) is directly related to the volatility of the plasticizer in use. Hence the

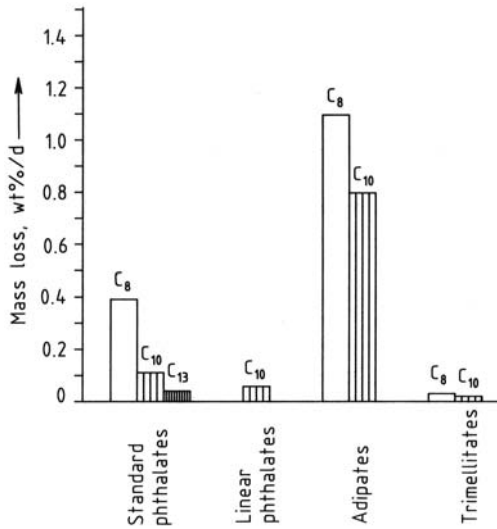


Figure 3. Volatile loss in use from plasticized PVC (50 phr plasticizer) for various plasticizers

higher molecular mass plasticizers give superior performance in this area. Figure 3 shows the percentage mass loss from plasticized PVC (50 phr of plasticizer) for various plasticizers at 100 °C. The superior performance of the trimellitate esters and inferior performance of adipate esters, relative to the phthalate, is illustrated.

For phthalate plasticizers thermal stability decreases in the order DTDPP > DIDPP > DINP > DOP > DIHP > DBP. Higher molecular mass esters such as trimellitates improve this still further and are used in demanding cable specifications which have strict mass loss requirements. Polyester plasticizers give the best performance in this area, with performance improving with increasing molecular mass. Additionally, branched esters have somewhat higher volatilities than their linear equivalents.

High-temperature performance also includes the generation of fume in the workplace, for which the same structure relationships apply. Not only does excessive plasticizer volatilization have environmental consequences but inaccuracies in formulation can be incurred since not all the plasticizer enters the PVC resin, resulting in a harder material than calculated.

Plasticizer molecules can undergo thermal degradation at high temperature. Esters based on the more branched alcohol isomers are more susceptible to such degradation. This can, however, be offset by the incorporation of an antioxi-

idant, and plasticizer esters for cable applications frequently contain a small amount of antioxidant.

4.2.3. Low-Temperature Performance

The ability of plasticized PVC to remain flexible at low temperature is of great importance in certain applications (e.g., external tarpaulins, underground cables). For this property the choice of the acid constituent of the plasticizer ester is of major importance, with the linear aliphatic adipic, sebacic, and azelaic acids giving excellent low-temperature flexibility compared to the corresponding phthalates and trimellitates.

There is also a major contribution to low-temperature performance from the alcohol portion of the ester; the greater the linearity of the plasticizer the greater the low-temperature flexibility. Figure 4 shows the cold flex temperature (the lowest temperature at which a sample of flexible PVC of standard dimensions can be twisted by 200° in the Clash and Berg test) for various PVC – plasticizer combinations. The increasing low-temperature performance with increasing alkyl chain length is illustrated, as is the superior low-temperature performance of the adipate esters.

4.2.4. Gelation Properties

The gelation characteristics of a plasticizer are related to its efficiency, and both properties are

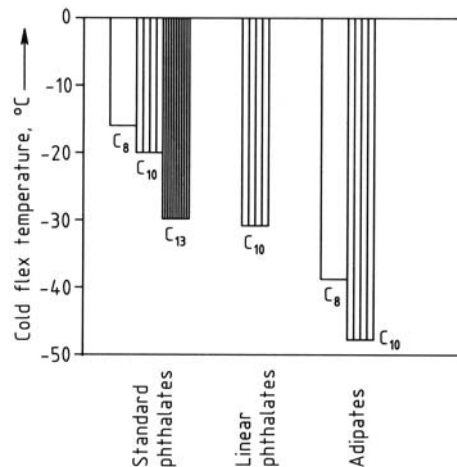


Figure 4. Cold flex temperature for various PVC – plasticizer combinations (50 phr plasticizer)

often discussed together. The gelation characteristics are a measure of the ability of a plasticizer to fuse with the polymer to give a product of maximum elongation and softness (i.e., maximum plasticization). Gelation properties are often measured either (1) as a processing temperature – the temperature to which the plasticizer and polymer must be heated in order to obtain these properties or (2) as a solution temperature, the temperature at which a grain of polymer dissolves in excess plasticizer, giving a measure of the solvating power of the plasticizer. Ease of gelation is related to plasticizer polarity and molecular size. The greater the polarity of a plasticizer molecule the greater the attraction it has for the PVC polymer chain and the less additional energy, in the form of heat, is required to cause maximum plasticizer – PVC interaction. The most active plasticizers are able to bring about these effects soon after the T_g of the polymer (70 – 80 °C) is reached, whereas the less active plasticizers require temperatures of ca. 180 °C for maximum elongation properties to be obtained. The polarity of the plasticizer is determined by both acid type and alcohol chain length. Aromatic acids, being of greater polarity, tend to show greater ease of gelation than aliphatic acid esters.

Molecular size also has a key contribution and explains why molecules of similar polarity can show different gelation properties. The smaller the plasticizer molecule the easier it is for it to enter the PVC matrix; larger molecules require more thermal energy to establish the desired interaction with the polymer. Since branching influences molecular size, this too has a contribution to gelation properties, with the more branched isomers showing greater activity. Thus for the phthalate esters ease of gelation decreases in the order BBP > DBP > DIHP > DOP > DINP > DIDP > DTDP. Figure 5 shows the greater ability of the more molecularly compact plasticizers to impart full gelation properties (i.e., maximum tensile strength).

4.2.5. Migration and Extraction

When plasticized PVC comes into contact with other materials, plasticizer may migrate from the plasticized PVC into the other material. The rate of migration depends not only on the plasticizer employed but also on the nature of the contact material.

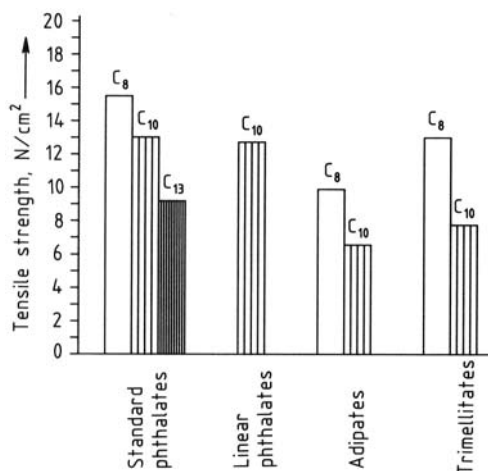


Figure 5. Tensile strength of various PVC – plasticizer combinations at 160 °C (50 phr plasticizer)

Plasticizer can also be extracted from PVC by a range of solvents, including water. How aggressive a particular solvent is depends on its molecular size and its compatibility with both the plasticizer and PVC. Water extracts plasticizer very slowly, oils are slightly more aggressive, and low molecular mass solvents are the most aggressive.

The key characteristics for migration and extraction resistance is molecular size. The larger the plasticizer the less it tends to migrate or be extracted. The extreme case is seen by the use of polymeric plasticizers in applications where excellent migration and extraction resistance is required. There is also a contribution from the linearity of the alcohol component of the plasticizer ester. The greater the linearity of the ester the greater its migration and extraction rate in comparison to the more branched isomers. Figure 6 shows the results of a standard test for the migration of plasticizer into rigid (unplasticized PVC). Equivalent masses of plaques containing different plasticizers were sandwiched between two rigid PVC discs and the plasticizer migration into the rigid PVC after the test was measured. The improved performance of the longer-chain esters and the trimellitate esters is illustrated.

4.2.6. Plastisol Viscosity and Viscosity Ageing

Plastisol viscosity and viscosity ageing are of great importance in emulsion PVC applications.

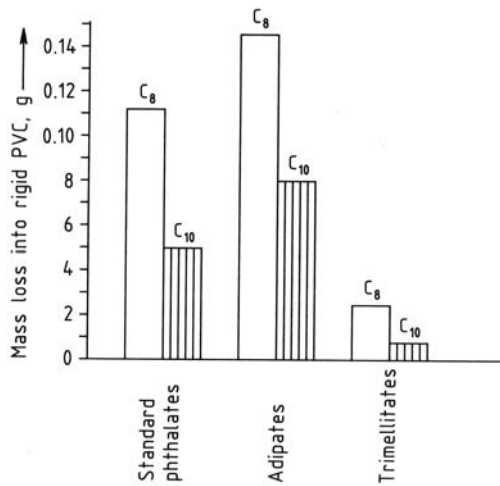


Figure 6. Mass loss into rigid (unplasticized) PVC (11d at 70 °C)

Plastisol viscosity, for a given emulsion PVC resin, has a strong dependence on plasticizer viscosity, with the lower molecular mass and more linear esters showing the lowest viscosity and hence the lowest plastisol viscosity (i.e., plastisol viscosity, for a common set of other formulation ingredients, increases in the sequence DBP < DIHP < DOP < DINP < DIDP). In spite of these viscosity differences, however, if plastisols are formulated to equal softness, i.e., taking into account the efficiency of the plasticizers involved, more of the less efficient plasticizer must be employed to impart the same softness to the product being manufactured. The addition of this extra liquid to the plastisol may produce an equivalent viscosity to that of the plastisol with the less viscous plasticizer. Esters based on aliphatic acids, being of lower viscosity than the corresponding aromatic acids, show lower plastisol viscosities, and adipate esters have found widespread use in plastisol applications although to meet other requirements (e.g., volatility, gelation characteristics) they are often employed in a blend with other esters.

Plastisols are often mixed and then stored rather than processed immediately. It is of great importance in this case for the plasticizer to show little or no paste thickening action at the storage temperature, and clearly in this instance it is not advisable to use a plasticizer of too great an activity, since grain swelling, leading to plastisol viscosity increase, can occur at low temperatures

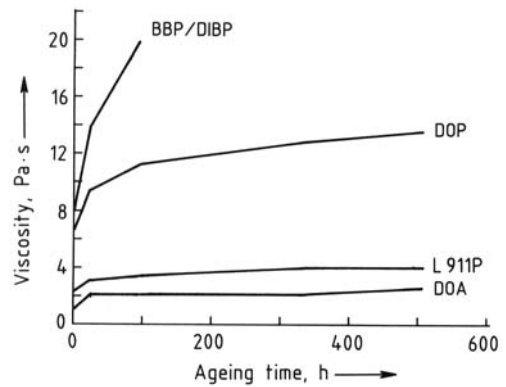


Figure 7. Viscosity ageing of PVC plastisols at 23 °C

for some active plasticizer systems. Figure 7 compares the ageing of plastisols based on various plasticizers. The molecularly compact plasticizers such as BBP and DIBP can enter the PVC matrix easily and cause a rapid increase in viscosity with time. The ageing characteristics improve as the polarity of the plasticizer is reduced. Greater linearity of the plasticizer (e.g., 911 phthalates) also improve this further, with adipates also showing very good viscosity stability.

4.2.7. Windscreen Fogging

The phenomenon of car windscreen fogging has been known for some time. Fogging is the condensation of volatile material on the car windscreen causing a decrease in visibility to the driver. Although this volatile material may arise from a variety of sources (e.g., exhaust fume sucked in through the ventilation system), material from inside the car (e.g., crash pads, rear shelves) may also contribute to windscreen fogging on account of the high temperatures which can arise in a car standing in sunlight. In the case of flexible PVC such a contribution may arise from emulsifiers in the polymer, stabilizers, and plasticizers. In each case manufacturers have studied their products in detail and now recommend low-fogging polymers, stabilizers, and plasticizers. Tests have been designed (e.g., DIN 75 201) to assess the fogging performance of both the PVC sheet and the raw materials used in its production. These tests involve heating a sheet of raw material for a specified period at a set

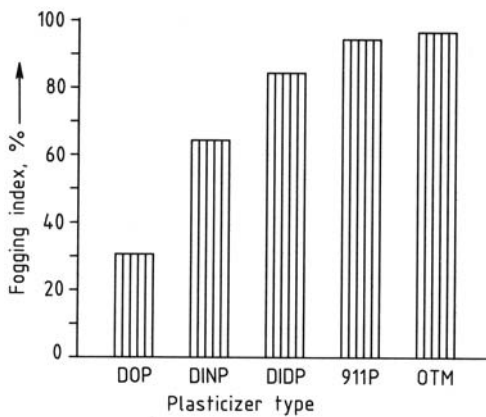


Figure 8. Fogging index of various plasticizers (6 h at 90 °C)

temperature in an enclosed apparatus with a cooled glass plate above the sheet or raw material. The reflectance of the glass plate before and after the test is then compared to ascertain the degree of fogging. Figure 8 shows the relationship between plasticizer molecular mass and linearity with fogging performance. The test was carried out at 90 °C for a 6 h duration (a variety of tests, each with their own specified temperature and time, are in use). In such a test, the fogging performance of a plasticizer is related to its

(1) volatility, (2) refractive index, and (3) surface tension. The precise nature of (2) and (3) is somewhat complex [33] and attempts to improve the test are currently in progress. In the case of plasticizer volatility it is clear that a higher concentration of plasticizer leads to increased fogging in the test. The higher molecular mass and more linear plasticizers give superior performance, and trimellitate esters (in suspension PVC applications) and L911 phthalates, with their high degree of linearity, and consequently low viscosity for plastisol applications, have achieved widespread use as low-fogging plasticizers for these applications.

4.2.8. Summary

Table 2 gives a summary of the properties described above. For each criterion the effect of (1) increasing plasticizer concentration, (2) increasing the size of the plasticizer molecule, (3) increasing the linearity of the plasticizer molecule, and (4) changing the acid constituent of the ester is discussed. A tick indicates improved performance, a cross indicates poorer performance, and a dash indicate no effect; ticks and crosses in parentheses indicate that any changes tend to be marginal.

Table 2. Summary of the effect of plasticizer choice on the properties of flexible PVC

Property (at equal softness)	Increased concentration	Increased size	Increased linearity	Acid used*
Efficiency (higher)	—	×	✓	ph=ad>tr
High-temperature properties	×	✓	✓	tr>ph>ad
Low-temperature properties	✓	✓	✓	ad>ph=tr
Gelation temperature	(✓)	×	(×)	ph>ad≥tr
Migration/extraction	×	✓	×	tr>ph>ad
Plastisol viscosity	✓	(✓)	✓	ad>ph
Plastisol ageing	—	✓	(✓)	ad>ph
Fogging	×	✓	✓	tr>ph>ad
Price	✓	✓	×	ph>ad>tr

*ph=phthalate; ad=adipate; tr=trimellitate.

It can be seen from this section that there is clearly no perfect plasticizer for every application: choice will depend on the performance requirements of the article being manufactured and additionally price.

5. Plasticization of Polymers other than PVC

5.1. Requirements for Plasticization

The plasticization of PVC accounts for the vast majority of plasticizer sales. However, significant amounts of plasticizers are used in non-PVC polymers and this may become increasingly important in the future. Although PVC is unique in its ability to accept and retain large quantities of plasticizer, effective plasticization of other resins with slightly modified plasticizers may be possible if certain conditions, specific to the polymer, are met.

The factors which must be considered for the plasticization of a polymer are

1. The need—even though some polymers may be compatible with large concentrations of plasticizer the resultant softening may be of little use
2. Short- and long-term compatibility—the ability of a polymer to accept and retain the plasticizer

For a plasticizer to enter a polymer structure the polymer should be highly amorphous (e.g., crystalline nylon will retain only a small quantity of plasticizer if it retains its crystallinity). Once it has penetrated the polymer the plasticizer fills free volume and provides polymer chain lubrication, increasing rotation and movement.

The plasticizer content of a polymer may be increased by suppressing crystallization in the polymer, but if crystallization subsequently occurs the plasticizer is exuded. For highly crystalline resins, the small amounts of plasticizer allowable can change the nature of the small amorphous regions with a consequent change in properties.

Plasticizer compatibility has been studied in many resins and a summary of these studies is given in [4].

5.2. Plasticization of other Polymers

Acrylic Resins. Although considerable information of the plasticization of acrylic resins is available, the subject is complicated by the fact that acrylic resins constitute a large family of polymers rather than a single polymeric species. An infinite variation in physical properties may be obtained through copolymerization of two or more acrylic monomers selected from the available esters of acrylic and methacrylic acid [34].

Plasticizers are used in the acrylics industry to produce tough, flexible coatings. Compatibility with common plasticizers are up to 10 wt %, although in some cases (for low molecular mass plasticizers) it can be higher (e.g., a formulation of 100 phr PMMA, 150 phr DBP, 225 phr chalk, 25 phr resorcinol has been used [4]). PMMA is used in small amounts with PVC. Cast acrylics, however, require a high glass transition temperature and high rigidity, hence no plasticizer is required.

Listed plasticizers include all common phthalates and adipates.

There has been interest in the development of acrylic plastisols similar to those encountered with PVC. Clearly the same aspects of both plastisol viscosity and viscosity stability are important. Patents appear in the literature [35] indicating that the number of available plasticizers which show both good compatibility with acrylic resins and satisfactory long term plastisol stability may be fewer than those showing equivalent properties with emulsion PVC resins.

Polyamides. The high degree of crystallinity of polyamides means that plasticization can occur only at very low levels. Plasticizers are used in nylon but are usually sulfonamide based since these are generally more compatible than phthalates (DEHP is 25 phr compatible, other phthalates less so; sulfonamides are compatible up to 50 phr).

Poly(Ethylene Terephthalate) (PETP) is crystalline and hence difficult to plasticize. Additionally, since PETP is used as high-strength film and textile fiber, plasticization is not usually required, although esters showing plasticizing properties with PVC may be used in small amounts as processing aids and external lubricants. Plasticizers have also been used to aid the

injection molding of PETP, but only at low concentrations.

The main interest in plasticizers for PETP is in dyeing. Due to its lack of hydrogen bonds PETP is relatively difficult to dye. Plasticizers can increase the speed and intensity of dyeing. The compounds used, however, tend to be of low molecular mass since high volatility is required to enable rapid removal of plasticizer from the product.

Polyolefins. Interest has been shown in the plasticization of polyolefins [4], but their use generally results in a reduction of physical properties [16], and compatibility may be only 2 wt %. Most polyolefins give adequate physical properties without plasticization.

Plasticizers have been used with polypropylene to improve its elongation at break [15], although the addition of plasticizer can lower the glass transition temperature, room-temperature strength, and flow temperature. This can be overcome by simultaneous plasticization (ca. 15 wt %) and cross-linking. Plasticizers used include DOA.

Polystyrene is compatible with common plasticizers, but the modification of properties produced is of little value. Small amounts of plasticizer (e.g., DBP) are used as a processing aid.

Fluoroplastics. Conventional plasticizers are used as processing aids for fluoroplastics up to a concentration of 25 %. However, certain grades of Kel-F (polychlorotrifluoroethylene) contain up to 25 wt % plasticizer to improve elongation and increase softness. The plasticizers used are usually low molecular mass oily chloroethylene polymers [4].

Rubbers. Plasticizers have been used in rubber processing and formulations for many years [36], although phthalic and adipic esters have found little use since cheaper alternatives, e.g., heavy petroleum oils, coal tars, and other predominantly hydrocarbon products, are available for many types of rubber. Esters (e.g., DOA, DOP, DOS) can be used with latex rubber to produce large reductions in glass transition temperature. More polar elastomers such as nitrile rubber and chloroprene rubber are insufficiently

compatible with hydrocarbons and require a more specialized type of plasticizer, e.g., a phthalate or adipate ester. Approximately 50 % of nitrile rubber used in Western Europe is plasticized at 10 – 15 phr (a total of $5 - 6 \times 10^3$ t/a), and 25 % of chloroprene at ca. 10 phr (ca. 2×10^3 t/a). Usage in other elastomers is very low but may increase due to toxicological concerns over polynuclear aromatic compounds.

Work on the use of high molecular mass esters in nitrile rubber has compared DINP with DBP and showed that at the 10 phr the nitrile rubber was effectively plasticized with DINP [37].

6. Toxicology and Environmental Aspects

6.1. Toxicity Studies on Plasticizer Esters

Acute Toxicity. The acute toxicity (LD_{50}) of plasticizers is extremely low (>2000 mg/kg). For example, DOP has an oral LD_{50} of $>30\,000$ mg/kg.

In addition to their low acute toxicity many years of practical use coupled with animal tests show that plasticizers do not irritate the skin or mucous membranes.

Numerous long-term feeding trials on plasticizers have been carried out. The majority of these studies have been on di-2-ethylhexyl phthalate (DEHP, commonly called DOP) because it accounts for around 50 % of the plasticizer usage in Europe and has been considered as a model for the other phthalates. See also → Phthalic Acid and Derivatives, Section 6.2.5.).

Prior to 1980 such studies showed no adverse effects. However, in 1980 the results of a two-year feeding study carried out as part of the National Toxicology Program/National Cancer Institute (NTP/NCI) Bioassay Program in the United States indicated that DOP causes increased incidence of liver tumors in rats and mice and that di-2-ethylhexyl adipate (DEHA, commonly called DOA) had a similar effect in mice but not rats [38], [39]. In these studies the levels of plasticizers fed were very high, this being only possible because of their low acute toxicity. Their diets contained up to 12 000 ppm of DOP and 25 000 ppm of DOA (this is

comparable with a human consuming 0.5 L of DOA every day).

A large number of more recent investigations [40–43] carried out in both Europe and the United States on a variety of plasticizers and different types of animals clearly show:

1. Plasticizers are not genotoxic.
2. Oral administration of plasticizers, fats, and other chemicals (such as hypolipidaemic drugs) to rodents causes a large increase of microbodies in the liver called peroxisomes. This peroxisome proliferation is considered by some authors to be linked to the formation of liver tumors.
3. The administration of plasticizers, fats, or hypolipidaemic drugs to nonrodent species such as the marmoset (a primate considered to be metabolically closer to humans) does not lead to peroxisome proliferation and liver damage. Some commonly used hypolipidaemic drugs (e.g., clofibrate), which cause peroxisome proliferation in rodents, have been used by humans for many years with no ill effects.
4. These species differences have also been observed in *in vitro* studies on the liver cells of rats, mice, guinea pigs, marmosets, and humans. Peroxisome proliferation was observed in the rat and mouse cells but not in those of humans, marmosets, or guinea pigs.
5. On the basis of these differences in species response (especially if the extremely high exposure in the animal tests is also taken into consideration) it is concluded that plasticizers pose no significant hazard to humans.

Human Exposure to Plasticizers. Experimental investigations and assessments in the United States and Europe have shown that the average human intake of plasticizers amounts to 2 g per person per year. This is mainly due to traces of DOA migrating from food packaging. The level of exposure is considerably below the dose at which toxic effects are to be expected. The no observed effect level (NOEL) for DOA and DOP is ca. 40 mg per kilogram body weight per day, or higher depending on the kind of effect, i.e., at least 1000 g per year for an average adult. There is thus a 500 fold safety factor between the estimated plasticizer intake of 2 g per person per year and the NOEL. Taking into consideration

the difference in response between rodents and primates, the safety factor is in fact even greater.

The Opinion of Official Experts and Legislative Authorities. The IARC of the WHO has classified DOP as “an agent possibly carcinogenic to humans,” largely because of the NTP/NCI rodent studies. However, IARC has not classified DOP as a carcinogen for regulatory purposes [44].

The EC Working Group “Classification and Labeling of Dangerous Substances” has examined all the toxicological data and has concluded that DOP should not be labeled as a human carcinogen [45].

In Germany the Advisory Body for Environmentally Relevant Existing Substances (BUA) has summed up the situation in their report No. 4 (1986) as follows [46]:

“Chronic damages have been noticed in rodents exposed to high DOP concentrations (rat: over 40 – 70 mg per kg bodyweight per day). The rat because of a characteristic feature in its DOP metabolism – different from the human metabolism – is especially sensitive to this substance. Thus, data obtained via tests with these animal species have no relevance for man. Tests with primates – having a metabolism comparable to that of humans – showed that DOP was rather ineffective. According to these findings there is no basis to suspect chronic damages due to DOP exposure at environmentally relevant concentrations.”

Similarly the German Health Authority (BGA) has concluded that the carcinogenic effect of DOP in rats and mice is specific to this species and is not relevant to humans.

In the United States the FDA has not introduced any new regulations following the results of the NTP/NCI studies.

6.2. Plasticizers in the Environment

The release of plasticizers to the environment may occur during their production and distribution, during incorporation into PVC, and by loss from the finished article during use or after disposal.

The controlled nature of modern manufacturing processes makes it unlikely that significant loss of plasticizer to the environment occurs

during its production (measurements of total emission from a modern plasticizer plant have given values of less than 0.01 %).

The extremely low solubility of plasticizers in water means that little is lost by leaching from flexible PVC either during use or after disposal. The increasing use of modern incineration techniques to dispose of domestic waste results in complete combustion of plasticizers to carbon dioxide and water.

The main way in which plasticizers enter the environment is therefore by evaporation during processing with PVC. The extent of such losses depends on the process and plasticizer used and has been estimated to vary from 0.02 % for injection molding up to 1 % for coating processes. However, these levels are being continually reduced by the installation of incineration, scrubbing, and filtration systems in processing plants.

Plasticizers can be detected in the environment in the ultratrace (parts per billion) range.

There are no indications of an accumulation of plasticizers in water, soil, or air because they are biologically and photochemically degraded. Degradation is particularly rapid under aerobic conditions to produce carbon dioxide and water as for other organic substances.

The occurrence and effects of phthalates in the environment has been reviewed in detail by ECETOC (European Chemical Industry Ecology and Toxicology Centre) [47]. It is clear from this report that in laboratory tests microorganisms and fish can take up dialkyl phthalates; however, they are rapidly excreted and no toxic effects have been seen. The report concludes that at the levels corresponding to current use and disposal practices, phthalates do not represent a hazard to the environment.

Health Aspects of Flexible PVC. Small quantities of plasticizers may be lost from PVC by evaporation and extraction or by migration into other materials.

Plasticizer Evaporation From Flexible PVC. The use of plasticizers in the production of vinyl wall and floor covering can lead to plasticizer vapor being present in room air. However, the plasticizers used have extremely low vapor pressures and thus at 25 °C the maximum concentration of DOP is only ca. 0.01 mg/m³. The concentration of the higher molecular mass

plasticizers are even lower. Also, given the comparatively slow plasticizer release rate and normal ventilation, then the plasticizer concentration in reality is extremely low. The high concentrations sometimes reported must therefore be attributed to analytical errors. This is demonstrated by the fact that recent measurements of the air in an emission chamber containing 1 m² of PVC flooring for 96 h showed no detectable levels of plasticizer; the detection limit was 4 parts per billion.

Flexible PVC Toys. In the United States the Consumer Products Safety Commission (CPSC) has expressed concern that children might ingest plasticizers by sucking teething rings and pacifiers. The estimated intake of plasticizers by infants in this way varies over several orders of magnitude up to a maximum of 0.07 mg kg⁻¹ d⁻¹. On the basis of the toxicological evidence this does not represent a health risk. For other toys, such as balls and dolls, the intake of plasticizers is negligible. The use of plasticizers in PVC toys for infants is regulated in some countries.

Medical Uses of Plasticized PVC. Flexible PVC has been established for many years as one of the most important materials used in the manufacture of a wide variety of medical products. The main advantages of PVC are its low toxicity and its flexibility, clarity, and sealing properties. These permit the manufacture of lightweight, breakage-resistant medical devices that can be supplied ready for use in sterile packages.

It is known that low levels of DOP migrate from flexible PVC blood bags into blood. There is published evidence [48] showing that this has a beneficial effect in that it significantly reduces the destruction of red cell walls compared to that which occurs on storage in other plastic or glass systems. DOP is the only plasticizer authorized by the European Pharmacopoeia for use in the manufacture of PVC blood bags.

Plasticized PVC in Food Packaging. Flexible PVC is used to produce food wrap film, cap seals for bottles and jars, and tubing for beverages. DOP, DINP, and DIDP are used in caps and seals, whereas DOA and polymeric adipates are used in the production of food wrap film.

DOA is used in this application because it gives a film with a high degree of cling which remains flexible at low temperatures. It also provides the high permeability to oxygen and water vapor that is necessary to ensure good food storage.

The migration of plasticizer from these packaging materials into foodstuffs has been measured in the UK by the Ministry of Agriculture Fisheries and Food (MAFF) both for domestic and retail packaging of food. These measurements together with a knowledge of the typical diet has enabled MAFF to assess the maximum possible intake of plasticizers as 0.02 mg per person per day of phthalates and 8 mg per person per day of DOA [49]. These estimates are based on a worst case situation, which assumes that all solid foodstuffs are purchased wrapped in cling film and that 50% of these are subsequently rewrapped in the home.

The UK Committee on Toxicity of Chemicals in Food, Consumer Products, and the Environment (COT) has examined these data together with the relevant toxicological information and has concluded [50]:

“Toxic effects have been demonstrated for some plasticizers, but the safety margins between toxic doses and human intakes are large and we consider it very unlikely that there are any adverse health effects from the current or past use of plasticizers in food packaging materials.”

Recent CEFIC studies [51], [52] involving the administration to humans of deuterium-labeled DOA have established the major human urinary metabolites and their excretion rates. This, together with analysis of 24 h urine samples from a limited survey of the UK population, has shown the average DOA intake to be 3 mg per person per day. This is well below the tolerable daily intake of 18 mg per person proposed by the EC Scientific Committee for Food and hence again confirms the suitability of plasticized PVC film for all food contact applications.

Regulations and Provisions. In terms of handling and storage, plasticizers are in general classified as nonhazardous.

In different countries the recommended 8 h TWA limit for occupational exposure varies between 2 and 10 mg/m³.

These recommended exposure limits have been reviewed by the Health and Safety Authorities in the United Kingdom and Germany, and in

the light of recent toxicological findings they have confirmed that the current limits of 5 and 10 mg/m³, respectively, are satisfactory.

The regulations controlling the use of plasticizers in food contact applications differ from country to country. However, a common feature of the regulations is that plasticizer that migrates into foodstuffs should not have any adverse effects on their taste or smell and in general must not exceed 60 ppm. Because of the large volume of toxicological data indicating that phthalates and adipates pose no health risk to humans, regulatory authorities in most countries allow their use in caps, seals, tubing, and wrapping films.

6.3. Storage and Handling

Plasticizer esters are relatively inert, thermally stable liquids with high flash points and low volatility. Consequently they can be stored safely in mild steel storage tanks or drums for extended periods of time. Exposure to high temperatures for extended periods, as encountered in drums in hot climates, is not recommended since it may lead to a deterioration in product quality with respect to color, odor, and electrical resistance.

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