PLASTICIZERS

Introduction

A plasticizer is an additive that is mixed with a polymer in order to make it more flexible, durable, and processable by lowering the second-order transition temperature of the macromolecule. Plasticizers (1–3) are generally low molecular weight (M_w) resins or liquids, which form secondary bonds to polymer chains and spread them apart increasing the "free volume." Thus, plasticizers reduce polymer–polymer chain secondary bonding and provide more mobility for the macromolecules, resulting in a softer, more easily deformable mass.

Plasticizers are incorporated in the amorphous parts of polymers while the structure and size of any crystalline part remains unaffected. Plasticizers are expected to reduce the modulus, tensile strength, hardness, density, melt viscosity, glass transition temperature, electrostatic chargeability, and volume resistivity of a polymer, while at the same time increasing its flexibility, elongation at break, toughness, dielectric constant, and power factor. Ideal plasticizers should be highly compatible with the polymer, stable in both high and low temperature environments, sufficiently lubricating over a wide temperature range, insensitive to solar ultraviolet (UV) radiation, leaching, and migration resistant, inexpensive, and should fulfill health and safety regulations.

History of Plasticizers

The first known man-made plastic was manufactured in 1862 by Alexander Parkes in London, but it was not until the late 19th century when the concept of plasticizers was first introduced. In the early days, manufacturers of celluloid or celluloid lacquers used natural camphor and castor oil for plasticization purposes, but those were unsatisfactory for many end uses. The discovery of triphenyl phosphate in 1912, later used as substitute for camphor oil, was a significant turning point that ushered in the era of ester plasticizers. The most important product that resulted from this early discovery was tricresyl phosphate, which is still in use today. For some time, tributyl phosphate was highly regarded for cellulose derivatives, but it was eventually replaced by less volatile products. At the same time, glycerin acetates were developed but suffered the same fate due to their volatility. Phthalic acid esters found applications as plasticizers for the first time in 1920 and continue to be the largest class of plasticizers in the 21 st century. Dibutyl phthalate (DBP) gained a dominant position amongst plasticizers that it

held for many years and continues to hold today for polyvinyl acetate dispersions. Di(2-ethylhexyl) phthalate, DEHP or DOP, was introduced in 1930 and has been the most widely used plasticizer since the 1930 s. The driving forces for development of specialty plasticizers come from the extensive use of plastics in a wide range of applications, increased quality requirements, the need for materials that meet increasing rigorous product specifications, and compatibility problems relating to particular products. Food legislation, health and industrial safety, and commercial aspects play an important role and, over the last 50 years, have led to the development of the vast range of plasticizers currently available.

Theory and Mechanism of Plasticizer Action

Four general theories have been proposed to explain external plasticizer action. Some theories involve detailed analysis of polarity, solubility, interaction parameters, and the thermodynamics of polymer behavior, whereas others treat plasticization as a simple lubrication of chains of polymer from each other. An understanding of the plasticization process can be gained by combining ideas from each theory, and an overall theory of plasticization must include all these aspects.

   The steps involved in the incorporation of a plasticizer into a poly(vinyl chloride) (PVC) (see also VINYL CHLORIDE POLYMERS) product can be divided into five distinct stages:

   (1) *Adsorption step*: plasticizer is mixed with PVC resin.
   (2) *Adhesion step*: plasticizer penetrates and swells the resin particles.
   (3) *Absorption step*: polar groups in the PVC resin are freed from each other.
   (4) *Intermolecular plasticizing step*: plasticizer polar groups interact with the polar groups on the resin.
   (5) *Intramolecular plasticizing step*: the structure of the resin is reestablished, with full retention of plasticizer.

   Steps 1 and 2 can be described as physical plasticization, and the precise details of how this is carried out depends on the applications technology involved, ie, suspension or dispersion PVC. The rate at which step 2 occurs depends on the plasticizer viscosity, degree of branching, resin pore size and free volume, and particle size.

   Steps 3 and 4, however, can be described as chemical plasticization since the rate at which these processes occur depends on the chemical properties of molecular polarity, molecular volume, and molecular weight. An overall mechanism of plasticizer action must give adequate explanations for this as well as the physical plasticization steps.

   The importance of step 5 cannot be stressed too strongly, since no matter how rapidly and easily steps 1–4 occur, if plasticizer is not retained in the final product the product will be rendered useless.

   The Lubrication Theory.   The lubrication 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 to allow the plasticizer molecules to lubricate the chains. Once incorporated into the polymer, the plasticizer molecules shield the chains from each other, thus preventing the reformation of the rigid network (1).

The Gel Theory. This theory extends the lubrication theory by having the plasticizer break the resin–resin attachments of a three-dimensional honeycomb or gel structure and by masking these centers of attachment from each other, preventing their reformation. This gel is formed by loose attachments occurring at intervals along the polymer chain. This facilitates the movement of plasticizer molecules, thus imparting flexibility.

The Free Volume Theory. The free volume theory (see TRANSPORT PROPERTIES) is a further extension of the lubricity and gel theories and can be used to explain both external and internal plasticization. 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. Plasticizers increase the free volume of the resin and ensure that free volume is maintained as the resin–plasticizer mixture is cooled from the melt, preventing interactions between neighboring polymer chains. For the plasticized resins, free volume can arise from motion of the chain ends, side chains, or the main chain. The fact that free volume increases with molecular motion is useful in explaining internal plasticization achieved by side-chain addition, where each side chain acts as a small molecule and free volume of the system is increased.

The introduction of a plasticizer, which is a molecule of lower molecular weight than that of the resin, has the ability to impart a greater free volume per volume of material because there is an increase in the proportion of end groups and the plasticizer has a glass-transition temperature (T_g) (see GLASS TRANSITION) lower than that of the resin itself.

Thermodynamic or Mechanistic Theory. From the observation of migration of plasticized polymers it is clear that plasticizer molecules are not bound permanently to the polymer, but rather a dynamic equilibrium exists between solvation and desolvation of the polymer chains by plasticizer. Different families of plasticizers are attracted to the polymer by forces of different magnitude but the attraction is not permanent. There is a continuous exchange where a plasticizer molecule becomes attached to an active group on the polymer chain only to be dislodged and replaced by another plasticizer molecule.

Antiplasticization. Many resins tend to become more ordered and compact as existing crystallites grow or new crystallites form at the expense of the fluid parts of the amorphous material. For small additions of plasticizer, the plasticizer molecules may be totally immobilized by attachment to the resin by various forces. These tend to restrict the freedom of small portions of the polymer molecule necessary for the absorption of mechanical energy. This results in a more rigid resin with a higher tensile strength and base modulus than the base polymer itself. This phenomenon is termed antiplasticization. Above these low concentrations the polymer becomes plasticized.

Interaction Parameters.

The Hildebrand Solubility Parameter. This parameter, defined by δ (eq. 1), can be estimated based on data for a set of additive constants F, for the more common groups in organic molecules to account for the observed magnitude of

the solubility parameter:

$$\delta = \Sigma F / V \tag{1}$$

where V represents molar volume. Solubility parameters can be used to classify plasticizers of a given family in terms of their compatibility with PVC (2).

Polarity Parameter.   This parameter, defined by ϕ (eq. 2), shows a good correlation with plasticizer activity for nonpolymeric plasticizers. The parameter is defined as

$$\phi = [M(A_P/P_0)]/1000 \tag{2}$$

where M is the molar mass of plasticizer, A_P the number of carbon atoms in the plasticizer excluding aromatic and carboxylic acid carbon atoms, and P_0 the number of polar (e.g., carbonyl) groups present. The 1000 factor is used to produce values of convenient magnitude. Polarity parameters provide useful predictions of the activity of monomeric plasticizers but not activity of plasticizers from different families.

The Solid-Gel Transition Temperature.   This temperature or clear point, T_m, is a measure of plasticizer activity and is the temperature at which a single grain of PVC dissolves in excess plasticizer. The more efficient plasticizers show lower values of T_m as a result of their higher solvating power. This can be correlated with the ease of processing of a given plasticizer, with a control PVC resin.

The Flory–Huggins Interaction Parameter.   These ideas, based on a study of polymer miscibility (see also MISCIBILITY; SOLUBILITY OF POLYMERS), have been applied to plasticizers according to the following equation (eq. 3) in which V_1 is the molar volume of the plasticizer, obtained from molar mass figures and density values at T_m, A and B are system dependent constant and χ represents the interaction parameter.

$$1/T_m = A + B(1 - \chi)/V_1 \tag{3}$$

Specific Interactions.   Some mechanism of attraction and interaction between PVC and plasticizer must exist for the plasticizer to be retained in the polymer after processing. The role of specific interactions in the plasticization of PVC between the carbonyl functionality of the plasticizer was proposed on the basis of results from Fourier transform infrared spectroscopy. Reported shifts in the absorption frequency of the carbonyl group of the plasticizer ester to lower wave number are indicative of a reduction in polarity. These ideas have been extended using newer analytical techniques, in particular molecular modeling (qv) and solid-state nuclear magnetic resonance spectroscopy (NMR) (qv).

Types of Plasticizers

There are several possibilities to classify the plasticizers according to their physical-chemical properties. For example, according to their molecular weight

Table 1. Key Performance Grid and Corresponding Plasticizer Families

Family	General purpose	Performance plasticizers			Specialty plasticizers		
		Strong solvent	Low temp	Low volatility	Low diffusion	Stability	Flame resistance
Phthalates	X	X	X	X	X		X
Trimellitates			X	X	X		
Aliphatic			X				
dibasic esters			X				
Polyesters				X	X		
Epoxides			X	X		X	
Phosphates		X	X				X
Extenders	X						
Miscellaneous		X		X	X		

plasticizers can be classified as either monomeric or polymeric plasticizers. However, for a practical point of view, the plasticizers are preferentially classified regarding their chemical structure and their associated performance. The key performance grid and its corresponding plasticizer families are shown in Table 1.

The plasticizers are divided in three groups relating to their performance characteristics:

a. General Purpose (GP): due to their low production cost, these plasticizers are widely used to get the desired flexibility. Dialkyl phthalates with different alkyl groups, along with low cost oils called "extenders," appear within this group.
b. Performance Plasticizers (PP): these contribute secondary performance properties beyond the GP type. Performance criteria are "strong solvator," "low temperature," and "low volatility (LV)." Specific phthalates and other types of plasticizers, which present higher production costs, belong to this group.
c. Specialty Plasticizers (SP): this kind of plasticizer provides exceptional properties beyond those typically associated with flexible PVC designed for general purpose or specialty characteristics, such as "low diffusivity," "stability," and "flame resistance." A few specific phthalates, polyester plasticizers, epoxy plasticizers, phosphates, and halogenated plasticizers belong to this group. Obviously, the introduction of these plasticizers increases the production costs.

Phthalate Esters.   With more than 80% of the worldwide plasticizer market this family is by far the most widely used and produced class of plasticizers. As shown in Table 1, they contribute the most complete array of required performance properties in flexible PVC. Although phthalate esters can be prepared from many different alcohols, the range of alcohols used to make plasticizers for PVC applications is generally limited from C4 to C13 alcohols 3a,3b). Phthalate
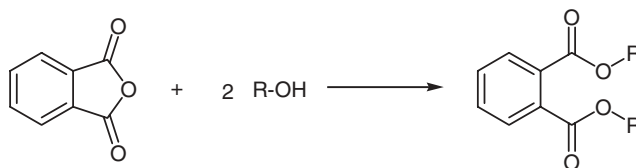
Fig. 1.   Synthesis of phthalate ester plasticizers.

esters prepared from alcohols below C4 are too volatile, while phthalate esters prepared from alcohols greater than C13 have limited compatibility. Many commercial grade phthalates are prepared using a mixture of monomeric alcohols, such as butanol with 2-ethylhexanol, or blends of linear heptanol, nonanol, and undecanol, and so forth. Di(2-ethylhexyl) phthalate (DEHP), which is prepared from 2-ethylhexanol, establishes the standard against which other plasticizers may be compared. Their synthesis is based on the esterification of one mole of phthalic anhydride and two moles of an appropriate alcohol (Fig. 1).

Extenders.   As shown in the general purpose plasticizer category they are most commonly employed with phthalates to reduce costs in general purpose flexible PVC (4). These low cost oils have limited compatibility in PVC; for example, naphthenic hydrocarbons may be used up to 35 weight% in dialkyl phthalate plasticizers, while aliphatic hydrocarbons are limited to less than 10%. Higher molecular weight phthalates are less tolerant of extender levels due to their reduced compatibility in PVC. Chlorinated paraffin extenders (5) are not widely used, but are commonly employed as secondary plasticizers worldwide. Chlorinated paraffins are produced by chlorination of hydrocarbons up to a chlorine content in the range of 30–70%. These secondary plasticizers are used to reduce cost and to improve fire resistance. The plasticizers with lower chlorine content have lower specific gravity, viscosity, and color, while higher chlorine content imparts increased fire resistance.

Citrate Esters.   Citrate esters have gained some importance as an alternative to DEHP in medical, toy, and food applications, due to their exceptional toxicological and/or environmental compatibility. Their synthesis is based on the esterification of citric acid with three moles of the corresponding alcohol. The citrate esters are less compatible, more volatile, more water sensitive, more difficult to fuse and more costly than DEHP. Higher-molecular weight citrates have also been suggested for use in automotive interior applications (6).

A list of the most employed commodity plasticizers can be found in Table 2.

Performance Plasticizers.   Performance plasticizers can be divided in three subgroups according to the desired secondary performance property: strong solvators, low temperature, and low volatility.

"Strong solvator" plasticizers are characterized by higher polarity and/or aromaticity. Thus, lower molecular weight phthalates such as dihexyl (DHP) and butyl octyl (BOP), as well as butylbenzyl (BBP) phthalate fall into this category; these plasticizers also contribute to volatile fuming during processing and volatilization in end use applications. In addition, there are non-phthalate plasticizers of high aromaticity that serve as strong solvators. Such materials are benzoate esters and tri(cresyl) phosphate.

Table 2. Commonly Used GP-plasticizers

Plasticizers	Carbon chain[b]	Molecular weight	Vapor pressure, Pa[a] (mm Hg @ 200°C)	Specific gravity 25°/25°C	Viscosity, mPa·s(cP) @25°C
Dinormalhexyl phthalate (DnHP)	(l)6	335	400	1.008	30
Diisoheptyl phthalate (DIHP)	7	362	280	0.983	30
Diheptyl phthalate (DnHP)	(l)7	362	253	0.983	30
Di(2-ethylhexyl) phthalate (DEHP)	8	391	173	0.982	58
Diheptylnonyl phthalate (DnHNP)	(l)7, (l)9	398	147	0.978	49
Dinormaloctyldecyl phthalate (DNODP)	(l)6, (l)8, (l)10	401	80	0.965	34
Diheptylnonylundecyl phthalate (DnHNUP)	(l)7, (l)9, (l)11	414	107	0.969	41
Diisononyl phthalate (DINP)	9	418	67	0.970	72
Dinonyl phthalate (DNP)	9	418	57	0.971	80
Dinormalnonyl phthalate (DnNP)	(l)9	418	43	0.967	39
Diisodecyl phthalate (DIDP)	10	447	47	0.964	88
Dinormalnonyldecylundecyl phthalate (DnNDUP)	(l)9, (l)10, (l)11	450	40	0.958	48
Dinonylundecyl phthalate (DnNUP)	(l)9, (l)11	458	40	0.954	50
Diundecyl phthalate (DUP)	(l)11	475	80	0.952	54
Diisoundecyldodecyl phthalate (UDP)	11, 12	502	20	0.955	185
Ditridecyl phthalate (DTDP)	13	530	11	0.951	160
Di(2-ethylhexyl) teraphthalate (DOTP)	8	391	160	0.981	63
Butylbenzyl phthalate (BBP)	4, 7	312	253	1.119	42
Diheptylnonyl adipate (DnHNA)	(l)7, (l)9	370	440	0.920	12
Di(2-ethylhexyl) adipate (DEHA)	8	370	307	0.924	14
Diisononyl adipate (DINA)	9	398	227	0.924	2.0
Diisodecyl adipate (DIDA)	10	426	77	0.916	25
Triheptylnonyl trimellitate (TnHNTM)	(l)7, (l)9	530	16	0.984	105
Tri(2-ethylhexyl) trimellitate (TOTM)	8	530	21	0.987	220
Triisononyl trimellitate (TINTM)	9	589	13	0.975	315
Di(2-ethylhexyl) sebacate (DOS)	8	426	131	0.911	25
Di(2-ethylhexyl) azelate (DOZ)	8	412	147	0.914	15

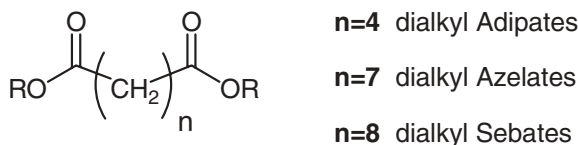[a]To convert Pa to mm Hg, divide by 133.3.
[b](l) is linear.

Fig. 2.   Chemical structure of dialkyl aliphatic esters.

"Performance Plasticizers at low temperature" are low temperature phthalates made with normal or "linear" alcohols. These less-branched alkyl groups contribute improved low temperature properties in all the chemical families of plasticizers. The entire family of *aliphatic dibasic esters* contributes exceptional low temperature properties. They are prepared by the esterification of one mole of dibasic carboxylic acid, such as adipic or azelaic acid, with two moles of monohydric alcohols. Lower molecular weight alcohols are used with higher molecular weight acids, and vice versa, such that the total carbon content per molecule ranges between C18 and C26. This maintains the apolar/polar ratio required to provide PVC compatibility along with low temperature properties. Di(2-ethylhexyl) adipate (DOA) is the standard and most widely used plasticizer in this class. Di(2-ethylhexyl) azelate (DOZ), di(2-ethylhexyl) sebacate (DOS), and diisononyl adipate (DINA) are used for low temperature applications requiring lower plasticizer volatility. Their chemical structures are shown schematically in Figure 2.

"Performance Plasticizers with low volatility" are low volatility plasticizers primarily because of their high molecular weight, which is also reflected in low vapor pressure. High molecular weight phthalates that serve as "LV" plasticizers include those having molecular weights greater than diisodecyl phthalate (DIDP). Increasing the molecular weight of phthalates increases the ratio of apolar/polar functionality until loss of PVC compatibility occurs at molecular weights greater than that of diisotridecyl phthalate DTDP. High molecular weight phthalates having low volatility and compatibility with PVC include diisoundecyl phthalate (DIUP), undecyl dodecyl (UDP), ditridecyl phthalate (DTDP) and diundecyl phthalate (DUP). Two further chemical families that belong to this category of low volatility plasticizers are trimellitates and polyesters.

Trimelliates.   These plasticizers are the product of three moles of monohydric alcohols and trimellitic anhydride (TMA) (Fig. 3). The third alkyl group, compared to phthalates, contributes higher molecular weight; the third ester group contributes sufficient polarity to maintain PVC compatibility. Common
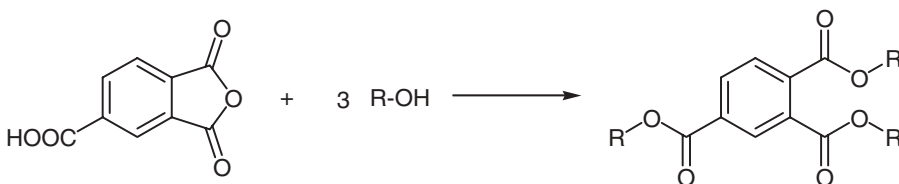

Fig. 3.   Synthesis of trimellitate esters from trimellitic anhydride.

esters in this family are tris(2-ethylhexyl) trimellitate (trioctyl trimellitate, TOTM); L79TM, an ester of mixed linear C7 and C9 alcohols; L810TM, an ester of mixed linar C8 and C10 alcohols, and triisononyl trimellitate (TINTM), an ester based on isononyl alcohol. They offer better moisture and water resistance than phthalates. As trimellitate esters are less volatile and have higher thermal stability and migration resistance, these plasticizers are used in automotive interior trim applications where windshield fogging is an issue. The lower migration rates of trimellitates have created additional demand for these products in gaskets (7).

Specialty Plasticizers.   Three different subgroups regarding to specialty characteristics are shown: plasticizers for low diffusion, plasticizers for stabilizing function, and plasticizers for fire resistance in PVC.

Plasticizers for Low Diffusion.   Low diffusivity is achieved by high molecular weight and highly branched isomeric structures. DIDP and DTDP impart improved resistance to diffusion-controlled plasticizer losses, and are sometimes used in combination with more costly diffusion-resistant plasticizers. But the polyester family is noted for its outstanding performance in this category.

Main representatives of these plasticizers of low diffusivity are polymeric and oligomeric plasticizers, typically polyesters, with a molecular weight range from 1000 to 8000. Polyethylene copolymers (Ethylene vinyl acetate (EVA), vinyl acetate ethylene (VAE), etc.) and terpolymers can range up to >500000. Polyesters are prepared by the esterification of propylene glycol or butylene glycol with aliphatic dibasic acids. The greater the plasticizer viscosity, or molecular weight, the greater its permanence. Polymeric plasticizers composed of branched structures are more resistant to diffusivity losses than those based on linear isomeric structures; on the other hand they are more susceptible to oxidative attack. The polarity, or the oxygen-to-carbon ratio, also impacts extraction resistance of the polymerics. Lower polarity materials exhibit better extraction resistance towards polar extraction fluids such as soapy water. Glutarate polymeric substances reportedly have a proven history of providing good weathering resistance. Upholstery and aircraft seating subject to extraction by body or hair oil are examples for useful applications. Refrigerator gasketing, electrical tape, decals, and oil-resistant electrical wire use high levels of polymeric substances frequently as the sole plasticizer.

Another typical class of plasticizers of low volatility and diffusivity are pentaerythritol esters. Pentaerythritol and dipentaerythritol are tetra and hexa alcohols, respectively; they are esterified with a stream of straight chain fatty acids to make plasticizers. Hercoflex 600 is the pentaerythritol tetraester and 707 is a mixture of tetra and hexa esters, using a mixture of pentaerythritol and dipentaerythritol. Their molecular weights are approximately 600 and 750, respectively, which contributes to both low volatility and diffusivity.

Plasticizers for Stabilizing Function.   The second type of specialty plasticizers, in addition to their plasticizing properties, act as thermal or photo-stabilizers. The most important representative of this group of additives are epoxidized vegetable oils that enhance thermal and UV stability of PVC. They are the only class of plasticizers that undergo a chemical grafting onto the PVC polymer at the site of labile chlorides in the presence of mixed metal stabilizers. This chemical family is composed of essentially two types of epoxidized natural products. Epoxidized

oils, such as soybean oil (ESO) and linseed oil (ELSO) are prepared by the use of peracetic acid, which adds the oxirane structure at unsaturated (double bond) sites. These oils have molecular weights of approx. 1000, causing them to perform as low volatility plasticizers. The other group of epoxy plasticizers is represented by octyl epoxy tallate (OET). This product results from the epoxidation of tall oil esters, which are the esterified product of tall oil acids. The OET has a molecular weight of approx. 410, and is a monoester. This causes it to have more limited compatibility in PVC and to contribute toward lower plastisol viscosity and low temperature properties. The primary performance attributes of epoxy plasticizers are their role in PVC stabilization, which is accomplished at less than 10 phr levels. Therefore, while they contribute to the plasticization in PVC, the secondary plasticizer effects are minimized.

Plasticizers for Fire Resistance in PVC.   The third class of specialty plasticizers is used when dealing with products with enhanced necessity of flame resistance. Flame resistant plasticizers include halogenated (preferably brominated) phthalates and the phosphate family. Brominated phthalate esters are produced by the esterification of tetrabromophthalic anhydride with various alcohols, most typically 2-ethylhexanol. Phosphate plasticizers that may be considered "inorganic esters" are prepared by the slow addition of phosphorous oxychloride to alcohol or phenol. The highly aromatic tricresyl phosphate (TCP) is the most effective fire retardant, but generates high smoke under fire conditions. Commercial phosphate plasticizers use combinations of aryl and C8 and C10 alkyl groups to offer a balance of fire reduction, volatility, and efficiency. A combination of phosphate plasticizers, antimony trioxide, and zinc borate yields a superior flame retardant grade of PVC for demanding applications such as plenum cable jacketing and electrical insulation.

Miscellaneous Plasticizers.   This group includes "phthalate-like" esters, benzoates, sulfonates, citrates, and similar materials. In the "phthalate-like" group, there are two isomers of DOP that are commercially available at similar costs of DOP. They are known as di(2-ethylhexyl) isophthalate (DOIP) "meta-isomer" and di(2-ethylhexyl) terephthalate (DOTP) "para-isomer." Di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH) is the corresponding hydrogenated product of diaromatic C9 phthalate ester (DINP). DINCH has recently been introduced by BASF as a candidate for specific applications with sensitivity for peculiar health and environmental concerns. The commercial name is Hexamoll. The processing disadvantages of DINCH can be seen through fusion property data. DOP, DOTP, and DINP will achieve fusion within 4 minutes at 300 °F (149°C) under certain test conditions, while DINCH requires an excess of 17 minutes (8).

Plasticizer Performance

The previous section summarized key plasticizer families and associated performance characteristics. Disciplined studies of carefully controlled model formulations, sample preparation, and conditioning have shown little correlation between neat plasticizer properties and their performance in PVC (9). It is well-known that reliable generalizations of plasticizer structure/performance relationships require extensive evaluations using disciplined model formulations, raw materials, sample preparation, and conditioning in the measurements and

cataloging of the data. As an example for such data we give in Table 3 a typical structure-properties-application relationship of different types of polymeric ester plasticizers.

Regarding plasticizer chemical structure as well as its concentration in PVC, the specific property requirements are influenced by:

– *Hardness (softness)* is significantly influenced by plasticizer "efficiency," which is related to plasticizer level and type of plasticizer.
– *Tensile strength and ultimate elongation* (% extension at failure) depend on plasticizer level; however there are not significant changes with respect to the type of plasticizer with PVC formulated to specified room temperature hardness.
– *Modulus* (stiffness, flexibility) may be measured under tensile stress (ASTM D 882) at a specified strain level, or under flexural stress (ASTM D 747), or under torsional stress (ASTM D 1043). This parameter significantly changes with plasticizer level, and is somewhat influenced by the type of plasticizers (efficiency) when measured at room temperature and formulated to specified hardness.
– *Low Temperature* properties (low temperature modulus and brittleness) significantly depend on plasticizer level and plasticizer family.
– The *color* of plasticized PVC compositions is typically not altered by the plasticizer. This is because most commercial grade plasticizers are near "water-white" in color. Highly colored (amber–brown) plasticizers would, of course, impart undesired color to flexible PVC compositions.

The effects of a wide variation in plasticizer level on the mechanical properties of PVC compounds are listed in Table 4.

Some physical properties appear to correlate with plasticizer performance in PVC only when the comparisons are restricted to a given plasticizer family and its homologues. Within each family, there are a variety of isomeric structures and homologues that contribute measurable variations in performance. According to alcohol and aromatic ring, the phthalate plasticizers family includes a great variety of isomers and homologues that are useful as plasticizers for PVC. For this reason, this plasticizer family is normally used as standards for the evaluation of the effects of chemical structure in PVC. Plasticizer performance effects have been differentiated as a function of five different degree of branching using commercial grade di(C8), di(C9), and di(C10) phthalates; these were grouped as:

– *Normal*: 100% unbranched; this group includes mainly academic product and limited commercial products based on mixtures of completely linear alcohol C6, C8, and C10. In the early 1960 s, synthetic straight-chain alcohols of even carbon numbers became available by the ethylene chain growth process (11) and the 610P and 810P products appeared on the market shortly afterwards.
– *Linear*: a mixture of normal and monomethyl branched alcohols. These monomethyl derived alcohols are synthesized by the hydroformylation of normal α-olefins. The resultant alcohol mixture has approximately a 70/30

Table 3. Polyester (Polymeric) Plasticizers: Composition, Properties, and Applications[a]

Dicarboxylic acid	Diol	Viscosity	Properties and applications
Adipic acid	1,2-Propane diol, 1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,6-hexane diol, neopentyl glycol	High, >10000 0 mPa·s (cP); medium, 4000–8000 mPa·s (cP)	High resistance to gasoline, oils, fats, and bitumen; migration-resistant; tubing, films, cable insulation, and jacketing
		Low, <4000 mPa·s (cP)	Oil and fat resistance markedly less satisfactory; for spread coating alone or in combination with high viscosity esters; other uses as above
Azelaic acid	1,2-Propane diol, 1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol	High, >10,000 mPa·s (cP)	High oil, gasoline, and fat resistance; adhesive tapes; other uses as for polysebacates
		Medium, 4000 to 8000 mPa·s (cP)	Easily processible; good compatibility; generally applicable polyester plasticizers
o-Phthalic acid	Ethylene glycol, 1,2-Propane diol, 1,3-Propane diol, 1,3-Butane diol, 1,4-Butane diol	Low, <4000 mPa·s (cP)	Easily processible; poor resistance to oils, fats, gasoline; reduced flexibility at low temperature
		<2000 mPa·s (cP)	Easy processing; for special applications
Sebacic acid	Ethylene glycol, 1,3-Propane diol, 1,3-Butane diol, 1,4-Butane diol, Neopentyl glycol	High, >10,000 mPa·s (cP)	Good resistance to gasoline, oil, fat, UV light; highly migration-resistant; good electrical properties; for high quality articles
		Medium, 4000–8000 mPa·s (cP)	Good compatibility with PVC, easily processible; for spread coating; protective clothing

[a]Source Ref. 10.

Table 4. Typical Properties of General Purpose Vinyl Plastic Products[a]

				Very flexible	Extremely flexible
DINP, phr	0	34	50	80	600
Wt% of composition	0	25	33	44	86
Typical properties					
Specific gravity, 20/20°C	1.40	1.26	1.22	1.17	1.02
Hardness Durometer A, 15 s	-	94	84	66	<10
Flexural stiffness[b] at 23°C					
MPa	>900	69	12	3.4	-
psi	>130,000	10,000	1,700	500	-
Tensile strength[c]					
MPa	>41	31	21	14	-
psi	>6,000	4,500	3,100	2,000	-
Elongation (%)[c]	<15	225	295	400	-
Brittleness[d]					
Softening temperature in°C	>23	−16	−32	−47	-
Softening temperature in °F	>73	+3	−26	−53	-
Examples	Bottles, pipe, siding, records	Shades, shoe heels, thin films, produce wrap	Wall-covering, book-binders, uphol-stery, garden hose	Boots, gloves, water beds	Fishing lures

[a]Source: see Ref. 1a, p. 149.
[b]ASTM D 747.
[c]ASTM D 882.
[d]ASTM D 746.

molar ratio of normal/monomethyl alcohols. These materials are typically 50–80% straight chain, generally an odd carbon number in length, and the balance made up of branched alcohols substituted at the C-2 position (12).

– *Slightly branched*: mainly is a mixture of monomethyl and dimethyl branched alcohols. The commercial slightly branched alcohols are produced by the hydroformylation of octenes. The resultant alcohol (nonanol) is a random mixture of monomethyl octanol derivates and dimethyl heptanols.

– *Moderately branched*: primarily dimethyl or monoethyl (ie, 2-ethylhexyl) branched alcohols. They are produced by the hydroformylation of mixed olefins (hexenes, heptenes, and octenes). These olefins are generated by the dimerization of a mixture of propylene and normal butane feeds and purified by distillation. The mixture of nonanol (hydroformylation of octenes) is mainly composed of dimethyl substituted C7 alcohols.

–   *Highly branched*: primarily trimethyl branched alcohols; 3,5,5-trimethylhexanol is the most representative alcohol of this group, which is synthesized by hydroformylation of branched pentenes.

These variations in degrees of branching demonstrate measurable effects on PVC properties with respect to plasticizing efficiency, low temperature properties, diffusivity, volatility thermal stability, and oxidative degradation. Investigations of structural effects (degree of branching) with C9 phthalates show that less branched isomers offer improved plasticizing efficiency, low-temperature flexibility and volatilization properties (13,14).

Preferred *general purpose* plasticizers range in molecular weight from diisoheptyl phthalate (DIHP) ($M_w = 362$) to DINP (418); DOP (390) appears in the middle of this group. The volatility of plasticizers dictates the preferred choice of the general purpose plasticizers for given applications. Therefore, two isomers of DOP have similar overall performance in PVC, except for a slight indication of being less compatible. Both isomers have novel resistance to migration into F2 nitrocellulose. They are known as DOIP (di 2-ethylhexyl) isophthalate, "isomer meta") and DOTP (di 2-ethylhexyl terephthalate, "isomer para").

Performance plasticizers having *strong solvating* characteristics include phthalates having higher polarity and aromaticity. These chemical structures also have higher volatility due to smaller nonpolar tails.

The structural features that contribute improved *low temperature* properties typically impart lower plastisol viscosities. Due to their own lower viscosity, their reduced tendency for solvation of PVC resin contributes to improved viscosity stability. However, these kinds of plasticizers impair compatibility in PVC and their loss in end use applications (by diffusion). It is shown that for given alkyl structures, the trimellitate family provides similar or only slightly improved low temperature properties vs. the phthalate counterparts, due to the lower plasticizing efficiency of trimellitates versus phthalates. Adipate plasticizers impart significantly improved low temperature properties versus their corresponding phthalate counterparts, in spite of the fact that they are more efficient in providing target room temperature hardness. The more linear alkyl structures in the plasticizers contribute improved low temperature properties. Other plasticizers such as OET and tri(2-ethylhexyl) phosphate, demonstrate performance characteristics similar to those of low temperature plasticizers. Epoxy plasticizers also enhance the thermal stability. For high molecular weight (about 1000) they enhance low volatility, while monoester OET increases low temperature performance. Finally, all dialkyl aliphatic esters, such as adipates, contribute exceptional low temperature properties.

Performance plasticizers with *low volatility* include plasticizers with higher molecular weight than DIDP ($M_w = 446$) and those of less branching degree (higher oxidative resistance). Linear alkyl structures contribute low temperature and lower volatility.

Applications Technology

Suspension PVC. These polymers are produced by suspending vinyl chloride in water and polymerizing this monomer using a monomer-soluble

Table 5. Typical Flexible PVC Formulations

Ingredient	Parts by weight	Parts per hundred resin (phr)	wt%
PVC	75	100	50
Plasticizer	45	60	30
Filler	26.25	35	17.5
Stabilizer	3	4	2
Lubricant	0.75	1	0.5
Total	150	200	100

initiator. PVC polymers produced via a suspension polymerization route have a relatively large particle size (typically 100–150 μm). Suspension polymers produced for the flexible sector have particles that are highly porous and are therefore able to absorb large amounts of liquid plasticizer during the mixing cycle. A typical flexible PVC formulation can be found in Table 5.

Using a ribbon blender, the resin, stabilizer, lubricant, and filler are heated to 70°C. The plasticizer is then distributed through piping running the length of the blender, and the heat remains on the jacketed blender until the dry point is reached. If the plasticizer is preheated, the dry point will be reached in less time. Polymeric plasticizers must be preheated to 70–80°C.

With a high speed mixer, set the jacket temperature at 90°C. Charge the resin and dry stabilizer, mix at high speed to 60°C. Add the plasticizer and other liquids and mix to the dry point at 70–85°C. Add the other solids and drop at 90–105°C with monomeric plasticizers. For polymerics, drop at 100–115°C. This dry blend can be either stored or processed immediately. Processing of suspension resin formulation is performed by a variety of techniques such as extrusion (qv), injection molding (qv), and calendaring (qv) to fuse the PVC and produce the end product.

The dry blend can also be extruded and the extrudate pelletized (qv) to produce pellets of PVC compound, which can then be reprocessed to produce the final article. This has the benefit of ease of processing and storage of raw materials since all the formulation ingredients are contained in the gelled compound.

Plastisols. Plastisol-forming polymers are produced by microsuspension polymerization or dispersion polymerization (15). Microsuspension produces very fine particles of monomer to ensure that small particle sizes of polymer are produced. In emulsion or dispersion polymerization (qv) the vinyl chloride is dispersed in a water-soluble initiator; the vinyl chloride particles are small and stabilized using surfactants. There are also several variations of these two basic techniques.

Much lower particle size resins are produced when compared to suspension resins (1 μm vs. 150 μm) with some residual surfactant from the polymerization process retained on the polymer. The small particle size imparts a lack of porosity to the resin and the demands on plasticizer behavior in a plastisol tend to be more complex. Choice of plasticizer is made with consideration given to the required viscosity of the plastisol and the required rheology (qv) of the plastisol. It is common to encounter formulations with two or three different plasticizers.
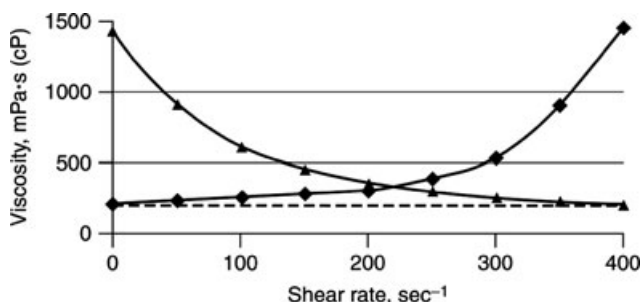
Fig. 4.   Rheological behavior.—Newtonian; dilatent; ▲ pseudoplastic.

Plastisols differ from their suspension analogues in that after mixing with plasticizer they produce a paste or plastisol, similar in appearance to paint, rather than a dry blend. For plastisols charge 80% of the liquids into the mixer. Start the agitator and add the solids in the following sequence: filler, blending resin, dispersion resin. At no time should the mix temperature reach 35 C°. This can be controlled through jacketing and the addition of some of the 20% of liquids originally held back. Take the mix through a high shear stage to break down the agglomerates. This will minimize viscosity buildup on aging due to plasticizer solvation. When there are no more lumps in the plastisol, add the remainder of the liquids and mix for homogeneity. The plastisol must be de-aerated before use, unless it is a foam plastisol. The plastisol can then be spread, coated, rotationally cast, or sprayed for processing.

Because the formulation ingredients in a plastisol are in liquid form, viscosity of the plastisol is of great importance and the intrinsic viscosity of the plasticizer contributes significantly to the plastisol viscosity, as does the precise polymerization conditions of the resin. The desired plastisol viscosity can be obtained by careful selection of polymer, plasticizer, and other formulation ingredients, but the shear rate applied to the plastisol also affects the viscosity. PVC plastisols are either (*1*) pseudoplastic, ie, viscosity decreases with shear; (*2*) near-Newtonian, ie, viscosity remains nearly constant with shear; or (*3*) dilatant, ie, viscosity increases with shear (see Fig. 4).

Plasticizer Efficiency.   This is a measure of the concentration of plasticizer required to impart a specified softness to PVC or shore hardness (Fig. 5). For a given acid constituent of plasticizer ester, ie, phthalate, adipate, etc., plasticizer efficiency decreases as the carbon number of the alcohol chain increases, eg, for phthalate esters efficiency decreases in the order: BBP > DIHP > DOP > DINP > DIDP > DTDP (16). In addition to size of the carbon number of the alcohol chain, the amount of branching is also significant; the linear plasticizers are more efficient. Choice of the acid constituent can also be significant. For equivalent alcohol constituents, phthalate and adipate esters are both considerably more efficient than their trimellitate equivalent.

High Temperature Performance.   High temperature performance in flexible PVC is related to plasticizer volatilization and plasticizer degradation. Plasticizer volatilization, both from the finished article during use at elevated temperatures (eg, in electrical cable insulation) and also during processing
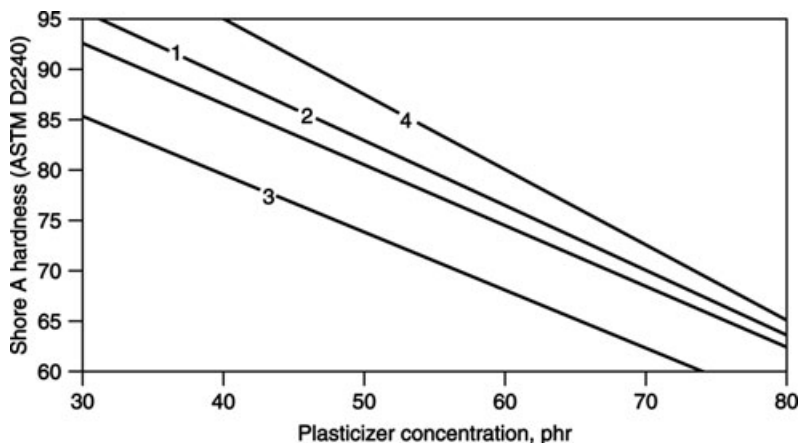
Fig. 5. Relative efficiency of plasticizers where (1) represents DEHP; (2) Palatinol 9P; (3) DEHA; and (4) TOTM. (Palatinol is a registered trademark of BASF and 9P is a linear C9 phthalate.)

[ie, release of plasticizer volatile organic compounds (VOCs)], is directly related to the vapor pressure and volatility of the plasticizer. The higher molecular weight phthalates give superior performance in this area. Higher molecular weight esters such as trimellitates are even less volatile and trimellitate esters find extensive use in the demanding wire and cable and automotive specifications, which have strict mass loss requirements. Branched esters have higher volatilities than their linear equivalents.

With regards to VOCs in the workplace, the same structure relationships apply. Not only does excessive plasticizer volatilization have environmental consequences, but since not all of the plasticizer in use enters the PVC resin this results in a harder material than anticipated. As a result of environmental protection legislation, more end users are looking at means of reducing or recovering and reusing plasticizer fumes and breakdown products.

Plasticizer molecules can undergo thermal degradation at high temperatures. Esters based on the branched alcohol isomers are more susceptible to such degradation because they have more tertiary carbon sites. With the addition of an antioxidant (topanol CA) to the plasticizer, its thermal properties can be improved.

Low Temperature Performance. The ability of plasticized PVC to remain flexible at low temperatures is of great importance in certain applications, eg, roofing, swimming pool liners, and tarpaulins. There is a significant 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. The choice of the acid constituent of the plasticizer ester is also important. The linear aliphatic adipic, sebacic, and azeleic acids give excellent low temperature flexibility compared to the corresponding phthalates and trimellitates.

Fusion. The fusion characteristics are a measure of the ability of a plasticizer to fuse with the polymer and develop maximum mechanical properties. Fusion properties are often measured either as a processing temperature or time

so as to obtain these properties. Ease of fusion is related to plasticizer branching and molecule size. The greater the branching of a plasticizer molecule, the greater attraction it has for the PVC polymer chain and the less additional energy, in the form of heat, is required. 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. Thus, for the phthalate esters ease of fusion rate decreases in the order BBP > DIHP > DOP > DINP > DIDP.

Plastisol Viscosity and Viscosity Stability.   After the primary contribution of the resin type in terms of its particle size and particle size distribution, plastisol viscosity has a secondary dependence on plasticizer viscosity. The lower molecular weight and more linear esters have the lowest viscosity and hence show the lowest plastisol viscosity. Esters based on aliphatic acids, being of lower viscosity than the corresponding aromatic acids, show lower plastisol viscosities. Adipate esters have found widespread use in plastisol applications in blends 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 viscosity stability at the storage temperature. It is not advisable to use a plasticizer of too great an activity, since grain swelling, leading to plastisol viscosity increase, can occur at room temperature for some active plasticizer systems.

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 but also on the nature of the contact material.

Plasticizers can also be extracted from PVC by a range of solvents, including water. The aggressiveness of a particular solvent 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 weight solvents are the most aggressive.

The key characteristic for migration and extraction resistance is molecular size. In general, the larger the plasticizer molecule the less it tends to migrate or be extracted.

Automotive Fogging.   The term automotive fogging relates to the condensation of volatile material on a car windshield causing a decrease in visibility where light hits it. Although this volatile material may arise from a variety of sources, materials from inside the car may contribute to windshield fogging because of the high temperatures that can be encountered inside a car in a dry hot climate. In the case of flexible PVC such a contribution may arise from emulsifiers in the polymer, lubricants, stabilizers, plasticizers, and coating on the modifier. In each case manufacturers have studied their products in detail and recommend low fogging polymers, lubricants, stabilizers, and plasticizers. Tests have been designed (SAE J 1756) to assess the fogging performance of both the PVC sheet and the raw materials used in its production. These tests involve heating of the sheet or raw material for a specified period at a set temperature in an enclosed apparatus with a cooled glass plate above the sheet or raw material. The reflectance of the glass plate is then compared before and after the test to ascertain the degree of fogging. In such a test, the fogging performance of a plasticizer is related to its volatility, vapor pressure, mass, and surface tension. The higher molecular weight and more linear plasticizers give superior performance. Trimellitate

esters and 911 phthalates, with their high degree of linearity and low viscosity for plastisol applications, are used as low fogging plasticizers for these applications.

Long-term Permanence. Outdoor weatherability is dependent on branching and a properly stabilized formulation. Typically, to determine the permanence of FPVC accelerated UV weathering and thermal stability, studies are performed in the laboratory and outdoor weathering studies are carried out in Arizona, Florida, and northern industrial climate such as in New Jersey or Ohio. The percent elongation retained and discoloration are the measurable criteria.

Health Aspects

Because of thermodynamic reasons, plasticizers tend to migrate to the surface of an article. On one hand, this leads to a progressive loss of its initial properties and, on the other hand, implies serious health hazards when PVC articles for biomedical applications such as intravenous bags and dialysis tubing or children toys are dealt with because additives migrated to the article's surface can contaminate physiological fluids like blood, serum, or plasma.

Phthalate plasticizers have been a target of worldwide scrutiny in the past two decades from consumer and environmental groups on the grounds of potential carcinogenicity and possible endocrine modulating effects. PVC-based medical plastics have received the most attention partly because medical uses constitute 10% of the phthalate plasticizer market. The PVC used in intravenous and blood storage bags typically contain 30–40 wt% DEHP and medical tubing such as dialysis tubing may contain as much as 80 wt% DEHP. This DEHP has been shown to leach out of PVC depending on temperature, amount of plasticizer present, agitation of the device, storage time while in contact with medical solutions, and the type of medium being stored in or moving through the medical device (17,18).

DEHP leaching from medical plastics was first observed in late 1960 s when Jaeger and Rubin (19,20) found that one pint of blood and its anticoagulant solution may contain 6 mg of DEHP after being stored in PVC blood bags for 21 days at 4–8°C. Another study by the same authors showed that DEHP was extracted from PVC blood bags by human blood at a rate of 2.5 mg/l per day at the typical blood bank storage temperature of 4–8°C. Extensive research began after the International Agency for Research on Cancer classified it as a "possible carcinogenic to humans" (21) in 1980 based on early studies on rodents. Subsequently, numerous experiments were conducted to examine the testicular and ovarian toxicity, as well as the embryotoxicity, nephrotoxicity, cardiotoxicity, pulmonary toxicity, and hepatotoxicity of DEHP in mammals. Results proved it to be a possible carcinogenic substance, but it has been found that the maximum safety limits required for consumer products are at least 75 times lower than a hazardous concentration (22).

Leaching of DEHP from plasticized PVC has been observed in soapy water, cottonseed oil, and also in high humidity environments. While losses in aqueous solutions are small, these percentages are not insignificant especially considering the lifetime exposure and bioaccumulation of DEHP. Particular concern has been

raised in neonatal care applications because newborns receive among the highest doses of DEHP from blood transfusions, extracorporeal membrane oxygenation, and respiratory therapy (23).

Using the typical PVC-DEHP tubing and EVA bags with PVC-DEHP connections, it has been found that infants and children receiving intravenous total parenteral nutrition (TPN) infused through PVC administration sets potentially receive considerable amounts of DEHP every day. DEHP is extracted from the bags and tubing due to the high solubility of DEHP in lipids. DEHP extraction by TPN depends on the lipid content of each TPN preparation and the flow rate(24).

Adults can also be subjected to DEHP exposure from medical plastics. A leachability study of DEHP from PVC haemodialysis tubing during maintenance haemodialysis of 10 patients with chronic renal failure was carried out. The patient blood obtained from the inlet and the outlet of the dialyzer was analyzed during a 4 h dialysis session. An average DEHP quantity of 123 mg was extracted from tubing during a single dialysis session, of which approximately 27 mg was retained in the patient's body (25).

Phthalates are also used in baby-care products and toys which represent around 1% of the phthalate plasticizer market. Since young children put the plastic-toys in their mouth, the plasticizers can leach out and be swallowed, which has led to the investigation of low toxicity plasticizers (26).

For all these reasons DEHP is one of several phthalate plasticizers that has been recently (February 10, 2009) banned by the U.S. Consumer Product Safety Commission (CPSC) for the manufacture of child care articles and toys containing phthalates (27).

Leaching and Migration

Leaching and migration of plasticizer molecules from polymers, independent of the health aspects mentioned above, is a critical issue that determines a material's usable lifetime. Leaching, by definition, refers to the removal of a substance from a solid via a liquid extraction media. Migration, on the other hand, refers to any method by which a component leaves a material—to a gas, liquid, or solid phase.

Plasticized polymers are often in contact with stationary or flowing fluids, or in contact with some other solid material. In the course of time, plasticizers tend to diffuse down the concentration gradient to the interface between the polymer surface and the external medium. In many instances, the interfacial mass transport to the surrounding medium has been found to be the limiting step rather than diffusion of plasticizer through the matrix to the surface. This rate is usually a function of temperature and initial plasticizer concentration while the rate of migration (permeation) is a product of solubility and diffusion coeficients. Whether the plasticizers leach out to a liquid, or migrate to gaseous or solid substance, polymers fail to retain their flexibility while the loss of plasticizers leaves the polymers inappropriate for the desired application. Leaching and migration issues are indeed one of the toughest challenges regarding research in the plasticizer industry today.

Research Trends for Avoiding Migration

Several approaches have been developed to reduce the leaching of plasticizers into physiological fluids as well as different organic and inorganic solvents and also to reduce the migration of plasticizers into solid and gaseous media (28). These techniques vary in level of complexity and also cost. Some methods that have successfully reduced leaching are described in what follows.

Surface Modification. Surface modification of polymers has attracted great attention in biomaterial research because it can improve the biocompatibility of a polymer without compromising the mechanical properties. This technique has also been employed to reduce or prevent leaching and migration of plasticizers from polymers.

Surface crosslinking is one of the most common techniques studied to prevent leaching and migration of plasticizers because the crosslinked polymer surface is supposed to act as a barrier to interfacial mass transport of plasticizer molecules. Crosslinking has, for example, been carried out by plasma treatments of PVC-based flexible films to limit plasticizer leaching from packaging into fatty foodstuffs. Best results were shown with Argon plasma (29).

Surface crosslinking of polymer to reduce leaching and migration is often employed along with other surface modification techniques. In fact, grafting of water soluble polymers to the surface of PVC films has been attempted using ionizing radiation from a ^{60}Co source(30). The leaching of the plasticizer DEHP into a strong organic extractant, n-hexane, can be significantly reduced.

Surface modification may also be achieved by wet-chemical treatments of PVC films using the possibility of substituting chlorine atoms by strong nucleophiles. Employing the classical Williamson ether synthesis reaction where the polymer is treated with an excess of sodium polyethylenglycolate (Na-PEG), leaching of DEHP to petroleum ether is reduced (31). The decrease in plasticizer leaching after PEG-grafting is presumably due to the hydrophilic PEG surface acting as a barrier to the diffusion of DEHP from the PVC matrix.

Another surface modification technique that has been found to be effective in preventing leaching of plasticizer is the nucleophilic substitution of chlorine in plasticized PVC by sodium azide in aqueous media and using tetrabutyl ammonium bromide as the phase transfer catalyst. The azidated PVC surface is then irradiated using UV rays with a 125 W lamp for various time periods to crosslink the surface. Nucleophilic substitution in order to surface-crosslink plasticized PVC may also be carried out with thiosulfate anions in aqueous media in the presence of a phase transfer catalyst (32). Tubes can then be sterilized by autoclaving and by gamma irradiation. This treatment resulted in a hydrophilic polymer surface, which showed significant leaching resistance for DEHP in hexane.

Surface Coating. Another possibility to reduce leaching and migration of plasticizers from the polymer surface is by coating the polymer surface with some non-migrating material (33). But these coatings are usually thick and may often cause a reduction in flexibility of the polymeric materials. However, a surface modification technique useful to prevent migration of plasticizers is chemical vapor deposition (CVD), which is generally used to coat complex substrates like

fibers or the inner surfaces of tubes. Usually, CVD requires high coating temperatures, which make it impossible to coat temperature-sensitive materials like PVC with titanium (Ti)-based layers. But a new plasma-assisted chemical vapor deposition (PACVD) process was developed to coat polymers at very low temperatures with Ti-based layers: PVC and five other commercial polymers were coated using the precursor $Ti[N(C_2H_5)_2]_4$ with the carrier gases hydrogen (H_2) and nitrogen (N_2) (34). The coating was found to be an effective diffusion barrier to prevent leaching of DEHP from PVC. Additionally, the Ti–C–N coatings have the potential to improve the blood compatibility of polymers.

Surface Extraction.   The removal of plasticizer from the polymer surface by surface extraction is another method proven successful at reducing diffusion and leaching in polymer systems. In surface extraction, a material is briefly exposed to a solvent for the plasticizer, and then dried. This leaves the polymer with a non-uniform distribution of plasticizer and a rigid surface that blocks interfacial mass transfer of the plasticizer. Such a treatment reduces the leaching of DEHP from plasticized PVC into liquid food or a stimulant by more than 50%, and also introduces a significant lag time for leaching. However, this rigid surface affects the flexibility of the polymer to some extent.

Internal Plasticization.   The most challenging strategy to solve any migration problems is the covalent linkage of the additive to the polymer chains. PVC can be chemically modified by nucleophilic substitution of its chlorine atoms. The internal plasticization of PVC by displacement of chlorine with phthalate-based thiol additives, that is, the covalent attachment of the plasticizer to the PVC chain has recently been described (35). Using this new class of plasticizers, the additive is linked via a thioether bridge to the PVC backbone (PVC-S-DOP). Good plasticization efficiency is achieved although flexibility is reduced compared with that of commercial PVC-phthalate systems. However, the migration is completely suppressed (Fig. 6).

Alternative Plasticizers.   Another approach to reduce plasticizer migration is to replace the classical plasticizers by materials that are biocompatible and/or have an oligomeric character (36). The most extensively studied polymeric materials for this approach are based on functionalized poly(ethylene oxide) (PEO) or poly(ε-caprolactone) or their combinations. According to the nature of these systems, the devices should be nontoxic. However, the migration of the plasticizers is still not completely avoided. Furthermore, crystallization or phase separations are possible, and the plasticizing efficacy is limited.

Ionic liquids (ILs).   ILs are a relatively new class of compounds that have been investigated as plasticizers for PVC (37) and poly(methyl methacrylate) (PMMA), and were found to be compatible with both polymer systems. ILs have low volatility, low melting points, a wide liquid range, are high-temperature stable, nonflammable, and are compatible with a wide variety of organic and inorganic materials. It was found that a number of imidazolium-, ammonium- and phosphonium-based ILs are capable of producing flexible PVC as does DEHP. Leaching of plasticizers from 20 wt% plasticized PVC samples to water showed much less leaching tendency than the widely used plasticizer DEHP. In a study of migration of plasticizers, phosphonium- and ammonium-based ILs showed excellent migration resistance (38).
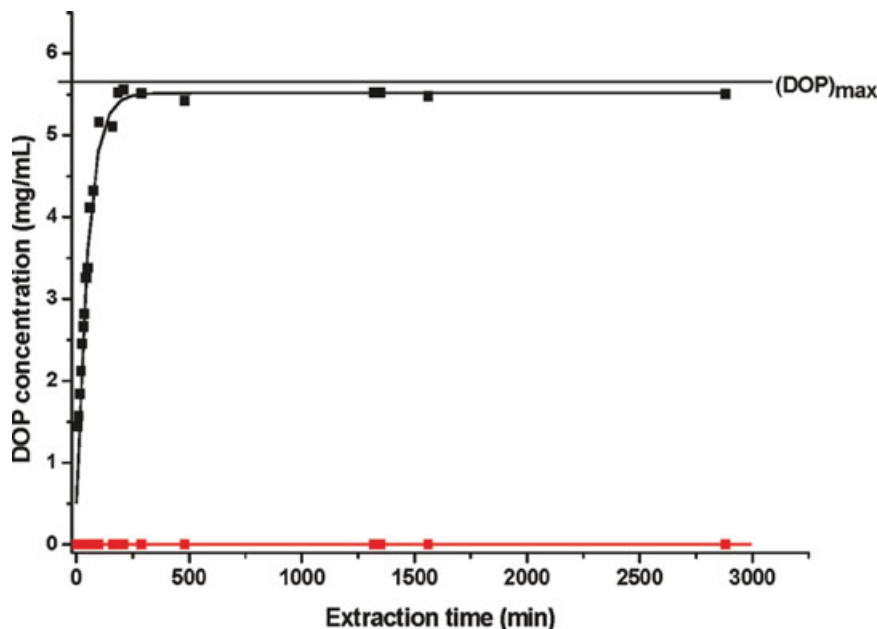
Fig. 6. Extraction of plasticized PVC sheets with heptane at room temperature: conventional PVC/DOP (black) and PVC-S-DOP (red). Reproduced with permission from Ref. 24. Copyright 2010, American Chemical Society

Economic aspects

In 2008, the worldwide consumption of plasticizers for flexible PVC was estimated at 5.6×10^6 Tons, in which 4.8×10^6 Tons were phthalate plasticizers (86% of the total produced volume) (39). Between 2005 and 2008, world capacity for plasticizers grew at an average annual rate of 4.7%, greatly outpacing world consumption, which grew at an average annual rate of 0.2% during the same period. Most capacity growth during 2005–2008 occurred in Asia-Pacific (mainly China), followed by Western Europe. Table 6 depicts a worldwide analysis of plasticizers consumption (40).

General economic conditions have strong influence on the demand for most downstream plasticizer markets. As a result, demand for plasticizers largely follows the patterns of the leading world economies. Figure 7 depicts the global plasticizer market breakdown in 2008 (40). The largest market segment is film and sheeting, followed by wire and cable. The primary factors, in this portion, regarding to plasticizers selection are low cost and ease of processing, with DOP

Table 6. Worldwide Plasticizer Market in 2008

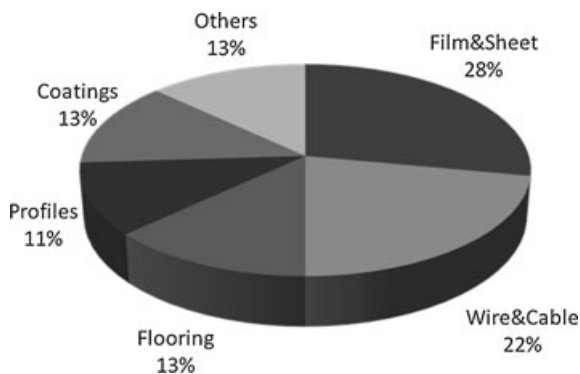| Region	USA	Europe	China	Rest Asia Pacific	Others	Total
Consumption	0.8 Mio. t	1.1 Mio. t	1.9 Mio. t	1.2 Mio. t	0.6 Mio. t	5.6 Mio. t

Fig. 7. Distribution of plasticizers into various applications. Reproduced with permission from Ref. 28

meeting this requirement in most parts of the world. The major end-use markets include construction-remodeling, automotive production and original equipment manufacturer. Communication and building wire and cable, film and sheet (calendared and extruded), coated fabrics and dispersions (flooring and other) are the largest markets for plasticizers.

The wire and cable market segment consume about 9×10^5 metric tons of plasticizers worldwide, having a variety of end-uses articles, including products for power transmission, buildings, automotive and communication cables. Normally, the primary factor in plasticizer selection is meeting the temperature rating of the wire at the lowest cost. With many other products, the testing required to ensure that the product meets the specification is based on an accelerated oven aging. To meet this requirement, most of the general purpose plasticizers can be used. Increasing the temperature rating, plasticizer selection moves towards higher molecular weight plasticizers such as DINP or DIDP. For highest temperature rating, trimellitates are often blended with higher molecular weight phthalates. PVC in wire and cable are potentially substituted by alternative materials. For the majority of the plasticized PVC products in the profile segment, general purpose plasticizers can be used. If low temperature flexibility improvement is needed, the general purpose plasticizers may be partially replaced with a linear plasticizer or adipate ester derivate such as dioctyl adipate (DOA).

In the coating segment, which also includes adhesive and sealant properties are a variety of plasticizers. The largest end-use for flexible PVC products within this segment is automobile underbody coatings. Plasticizer choices depend on production costs, fusion temperature requirements, and emissions. Many general purpose plasticizers meet those requirements.

The plasticizer consumption in the food and medical segment is small relative to the other segments. Plasticizer choice is usually restricted to a pre-approved list of chemicals for every particular application. Flexible PVC food film, for example, uses DOA, while many of the medical products use DOP as plasticizer. The actual goal of the legislation in the field of food contact materials is to keep food safe and wholesome by preventing any transfer of the constituents of food contact materials to food in such a way as to damage the foodstuff or present a health risk to the public. During the past decade governments and agencies in

Table 7. Market Share in USA, Western Europe, and Asia

Market share%	USA	Western Europe	Asia
DOP	12	19	65
DINP	23	32	18
DPHP/DIDP	19	23	<1
Linears/other phthalates	21	10	9
Non-phthalates	25	16	8

Europe and the U.S. have taken or proposed regulatory actions to limit exposures to DEHP, using a gradual shift from DEHP to alternative expected in medical applications.

In Table 7, the plasticizer consumption in USA, Western Europe, and Asia are summarized.

In 2008, phthalates accounted for almost 86% of world consumption of plasticizers and Asia had 65% of the global plasticizers capacity. Due to its overcapacity to produce the phthalate plasticizers against the corresponding demand, the expected market share will also increase because the key driver for future plasticizer growth in Asia is Oxo alcohol availability. The actual tendency to DEHP replacement by linear C9/C10 phthalates and alternative plasticizers in sensitive applications is taking place. During 2008–2013, continued discontinuation of production and consumption of several relatively minor phthalates will largely be negated by increased consumption of DPHP and DINP. The key success factor is related with the accessibility to C8/C10 plasticizers alcohols. World consumption of phthalate plasticizers is forecast to grow at an average annual rate of 1.6% during 2008–2013. World consumption of other phthalates is forecast to decline during 2008–2013; largely the result of declining demand for some phthalates, such as BBP and DBP, in many regions caused by regulatory issues and discontinued consumption of other relatively minor phthalates.

World consumption of phthalate plasticizers is forecast to grow at an average annual rate of 1.6% during 2008–2013. World consumption of other phthalates is forecast to decline during 2008–2013; largely the result of declining demand for some phthalates, such as BBP and DBP, in many regions caused by regulatory issues and discontinued consumption of other relatively minor phthalates.

World consumption of most other plasticizers (aliphatics diesters, trimellitates, epoxy, polymerics and phosphates) is forecast to grow at an average annual rate of 1.5–2.1% during 2008–2013, in line with general economic trends. Benzoates and specialty plasticizers (including citrates, sulfonates and miscellaneous "hydrogenated phthalates") are expected to grow rapidly during 2008–2013, albeit from a small base, largely because of replacement of several phthalates.

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