PLASTICIZERS

Introduction

A plasticizer is a liquid that is added to a material (usually a resin or elastomer) making that material softer, more flexible (by decreasing the glass-transition temperature T_g of the polymer), and easier to process. This broad definition encompasses the use of water to plasticize clay for the production of pottery, and oils to plasticize pitch for caulking boats. The most widely plasticized polymer is poly(vinyl chloride) (PVC) because of its excellent plasticizer compatibility characteristics. The development of plasticizers closely follows the development of this commodity polymer; however, plasticizers are also used with other polymer types.

The amount of plasticizer added to a polymer varies depending on the effect required. A small addition of plasticizer may be made to improve the workability of the polymer melt. This contrasts with large additions made with the specific intention of completely transforming the properties of the product. PVC without a plasticizer, ie, unplasticized PVC (PVC-U), is used in applications such as pipes, siding, and window profiles. With plasticizer added, articles such as automotive interior trim, jacketing, cable insulations, and PVC floorings are formed.

There are presently ∼300 plasticizers manufactured. Of these ∼100 are of commercial importance. A list of some common commodity and specialty plasticizers can be found in Table 1.

Types of Plasticizers

Two principal methods exist for softening a polymer to bring about the dramatic effects of plasticization. A rigid polymer may be internally plasticized by chemically

Table 1. Commonly Used Plasticizers

Plasticizers	Carbon chain	Molecular weight	Vapor pressure, Pa[a] (mm Hg @ 200°C)	Specific gravity 25° / 25°C	Viscosity, mPa·s(cP)@25°C
Dinormalhexyl phthalate (DnHP)	l6[b]	335	400	1.008	30
Diisoheptyl phthalate (DIHP)	7	362	280	0.983	30
Diheptyl phthalate (DnHP)	l7	362	253	0.983	30
Di(2-ethylhexyl) phthalate (DEHP)	8	391	173	0.982	58
Diheptylnonyl phthalate (DnHNP)	l7, l9	398	147	0.978	49
Dinormaloctyldecyl phthalate (DNODP)	l6, l8, l10	401	80	0.965	34
Diheptylnonylundecyl phthalate (DnHNUP)	l7, l9, l11	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)	l9	418	43	0.967	39
Diisodecyl phthalate (DIDP)	10	447	47	0.964	88
Dinormalnonyldecylundecyl phthalate (DnNDUP)	l9, l10, l11	450	40	0.958	48
Dinonylundecyl phthalate (DnNUP)	l9, l11	458	40	0.954	50
Diundecyl phthalate (DUP)	l11	475	80	0.952	54
Diisoundecyldodecyl phthalate (DUDP)	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)	l7, l9	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)	l7, l9	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, divided by 133.3.

[b]l is linear.

modifying the polymer or monomer so that the flexibility of the polymer is increased. Alternatively, a rigid polymer can be externally plasticized by the addition of a suitable plasticizing agent. The external plasticizing route is more common because of lower overall costs, and the use of external plasticizers allows the processor a certain degree of freedom in developing formulations for a range of products.

Internal Plasticizers.   There has been much dedicated work on the possibility of internally plasticized PVC (FPVC). However, in achieving this by copolymerization significant problems exist: (*1*) the affinity of the growing polymer chain for vinyl chloride rather than a comonomer implies that the incorporation of a comonomer into the chain requires significant pressure; (*2*) since the use of recovered monomer in PVC production is standard practice, contamination of vinyl chloride with comonomer creates additional problems, and (*3*) the complexity of the reaction can lead to longer reaction times and increased costs.

External Plasticizers.   There are two groups of external plasticizers, primary and secondary. A primary plasticizer, when added to a polymer, causes elongation and softness to be increased. These changes are brought about by mechanisms described in the following section. A secondary plasticizer, when added to the polymer alone, does not bring about these changes and may have limited compatibility with the polymer. However, when added to the polymer in combination with a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer. Secondary plasticizers are also known as extenders.

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, and 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 PVC product can be divided into five distinct stages:

(1) Plasticizer is mixed with PVC resin—adsorption step.
(2) Plasticizer penetrates and swells the resin particles—adhesion step.
(3) Polar groups in the PVC resin are freed from each other—absorption step.
(4) Plasticizer polar groups interact with the polar groups on the resin—intermolecular plasticizing step.
(5) The structure of the resin is re-established, with full retention of plasticizer—intramolecular plasticizing step.

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 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) 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:

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

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

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

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 (eg, 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, 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, and χ represents the interaction parameter.

$$1/T_\mathrm{m} = 0.002226 + 0.1351(1 - \chi)/V_1 \tag{3}$$

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 were 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 and solid-state nuclear magnetic resonance spectroscopy (nmr).

Molecular Modeling. A range of plasticizer molecule models and a model for PVC have been generated and energy minimized to observe their most stable conformations. Such models highlight the free volume increase caused by the mobility of the plasticizer alkyl chains. More detailed models have also been produced to concentrate on the polar region of the plasticizer and its possible mode of interaction with the polymer (3).
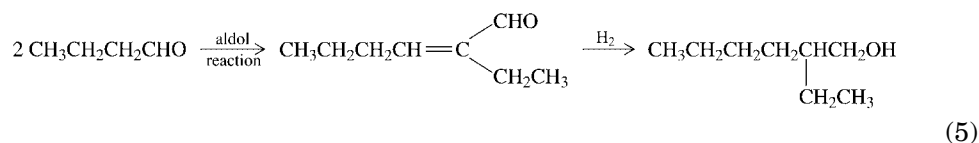
Solid-State Nuclear Magnetic Resonance Spectroscopy. Advances in technology have made the study of solids by NMR techniques of considerably greater ease. For the accumulation of solid-state ^{13}C nmr spectra, cross-polarization magic angle spinning (cpmas) can be utilized to significantly reduce signal-broadening effects present in solid state but not in the liquid state. The technique has been used to study the molecular effects of plasticization by comparing spectral shifts of PVC and plasticizer under various degrees of processing.

Phthalate Esters

The family of phthalate esters are the most abundantly produced worldwide. The plasticizer esters are produced from orthophthalic and terephthalic acid reacted with an appropriate alcohol (eq. 4). Phthalate esters are manufactured from methanol (C_1) up to C_{17} (4) alcohols although phthalate use as PVC plasticizers is generally in the range C_6 to C_{13}. Low molecular weight phthalates find use in nitrocellulose; higher phthalates as synthetic lubricants for the automotive industries.


$$\text{(4)}$$
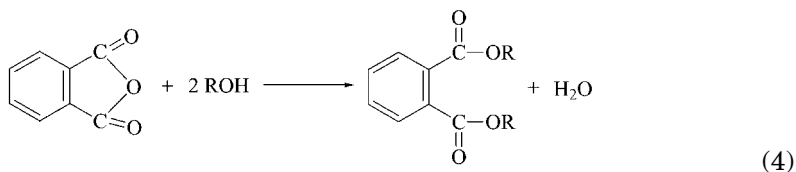
Di-2-ethylhexyl phthalate(DEHP) [117-81-7], also known as dioctyl phthalate (DOP), is generally considered as the industry standard. The reason for this is that it is in the mid-range of plasticizer properties. DEHP (or DOP) is the phthalate ester of 2-ethylhexanol, which is normally manufactured by the dimerization of butyraldehyde (eq. 5), the butyraldehyde itself being synthesized from propylene.

$$2 \ CH_3CH_2CH_2CHO \xrightarrow[\text{reaction}]{\text{aldol}} CH_3CH_2CH_2CH{=}C\overset{\displaystyle CHO}{\underset{\displaystyle CH_2CH_3}{}} \xrightarrow{H_2} CH_3CH_2CH_2CH_2\underset{\displaystyle CH_2CH_3}{CHCH_2OH}$$

$$(5)$$

The widespread use of this plasticizer is a reflection of its all-around general-purpose plasticizing performance and its properties, suitable for a great many standard products. It possesses good plasticizing efficiency, fusion rate, and viscosity which, coupled with a competitive price, make it attractive to the PVC compounder and processor.

Diisononyl phthalate and diisodecyl phthalate are produced by esterification of oxo-alcohols of carbon chain length 9 and 10. The oxo-alcohols are produced through the carbonylation of alkenes (olefins). The hydroformylation or carbonylation process (eq. 6) adds a carbon unit to an alkene chain by reaction with carbon monoxide and hydrogen with heat, pressure, and catalyst. In this way a C_8 alkene is carbonylated to yield a C_9 alcohol. Because of the distribution of the C=C double bond in the alkene and the varying effectiveness of certain catalysts, the position of the added carbon atom can vary and an isomer distribution is generally created in such a reaction. The nature of this distribution depends on the reaction conditions. Consequently, these alcohols are termed *iso-alcohols* and the subsequent phthalates *iso-phthalates*.

Another method of producing a nonyl alcohol, which has gained predominance in the past few years, is by the dimerization process. In this process *n*-butylenes react to form an octene. Then through hydroformylation the 8-carbon olefin is converted to a nonyl alcohol (eq. 6). This alcohol has specific branching and some linearity that provides the corresponding ester with improved properties over esters made from isononyl alcohol.

$$(6)$$
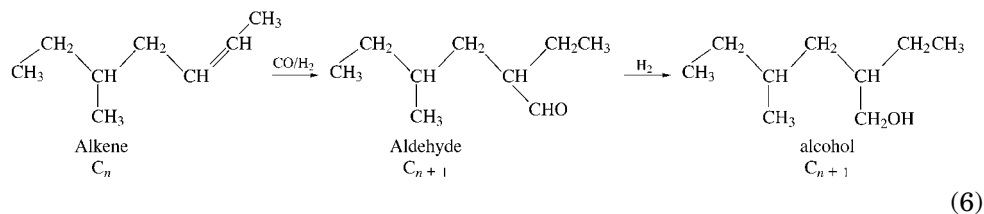
The C_9 and C_{10} phthalates (DINP, DNP, and DIDP) generally compete with DEHP as commodity general-purpose plasticizers. Other phthalates are available at opposite ends of the carbon number range [eg, diisohexyl phthalate (DHP, C_6) and diisotridecyl phthalate (DTDP, C_{13})], but these serve more specialty markets. The C_8 phthalate, diisooctyl phthalate (DIOP), is also a commodity plasticizer where it is used as an alternate to DEHP for environmental reasons.

The fourth process used to produce phthalate alcohols is the Ziegler process and the Ziegler displacement process. In the Ziegler process straight chain even-numbered carbon alcohols are produced from ethylene. Triethylaluminum is produced from aluminum, hydrogen, and ethylene. With the addition of more

ethylene the chain is lengthened in two-carbon increments. Oxidation and hydrolysis yield the primary even-numbered alcohols.
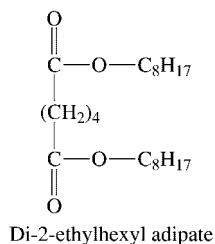
With the Ziegler displacement process the higher alkyl group is displaced from the chain growth product by ethylene. This yields a mixture of even-numbered linear alpha olefins with the trialkyl aluminum being recycled. The odd-numbered linear alcohols are produced through hydroformylation of the olefin and hydrogenation of the odd-numbered aldehydes.

The linear phthalates produced from these alcohols provide many advantages over their branched counterparts. Among these are processability, efficiency, volatility, viscosity, thermal stability, light stability, low temperature, and long-term permanence.

Citrate esters have gained some importance as an alternate to DEHP in medical, toy, and food applications. The citrate esters are more volatile, less compatible, more water sensitive, more difficult to fuse, and more costly than DEHP.
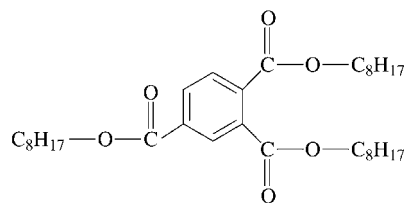
Adipate Esters

Alcohols of similar chain length to those used in phthalate manufacture can be esterified with adipic acid rather than phthalic anhydride to produce the family of adipate plasticizers. For example, esterification of 2-ethylhexanol with adipic acid yields di-2-ethylhexyl adipate (DEHA), also known as dioctyl adipate (DOA).

$$
\begin{array}{c}
O \\
\parallel \\
C - O - C_8H_{17} \\
| \\
(CH_2)_4 \\
| \\
C - O - C_8H_{17} \\
\parallel \\
O
\end{array}
$$

Di-2-ethylhexyl adipate

The family of adipic acid esters in PVC applications has improved low temperature performance relative to phthalates and lower plastisol viscosities, because of the lower inherent viscosities of the plasticizer. Adipates used are typically in the C_7–C_{10} range. Incompatibility problems can be encountered at higher carbon numbers, especially at high addition levels. Adipates are more volatile and have higher migration rates than phthalates. Because they are a specialty for the PVC industry, they are higher priced. As a result, it is not uncommon to encounter adipates used in blends with phthalates to produce a compromise of properties. Because of these limitations, linear phthalates are often used in place of adipates wherever possible.

Trimellitate Esters

These materials are produced by the esterification of a range of alcohols with trimellitic anhydride (TMA), which is similar in structure to phthalic anhydride with the exception of the third functionality (COOH) on the aromatic ring.

Tris-2-ethylhexyl trimellitate

Esters are produced in the ratio of 3 mol of alcohol to 1 mol of anhydride. Common esters in this family are tris-2-ethylhexyl trimellitate (trioctyl trimellitate, TOTM); L79TM, an ester of mixed linear C_7 and C_9 alcohols; L810TM, an ester of mixed linear C_8 and C_{10} alcohols; and trüsononyl trimellitate (TNTM), an ester based on isononyl alcohol.

In a flexible PVC compound the trimellitates are less volatile and have improved thermal stability over the phthalate and polymeric plasticizers. Their plasticizing effectiveness and compatibility are similar to phthalates. They offer better moisture and water resistance than the phthalates or polymeric plasticizers. Large volumes of trimellitate esters are used in 90°C and 105°C UL rated insulation compounds. Because of their extraction and migration resistance, thermal stability, and low volatility, the trimellitates are used in conjunction with 911P and DUP in automotive interior trim applications where windshield fogging is an issue.

Phosphate Esters

The principal advantage of phosphate esters is improved fire retardancy. The fire performance of PVC itself, relative to other polymeric materials, is very good because of its high halogen content, but the addition of plasticizers reduces this. Consequently, there is a need, in certain demanding applications, to improve the fire-retardant behavior of flexible PVC by reducing the limiting oxygen index (LOI) and smoke. Phosphate esters are combined with brominated phthalates for use in FPVC UL rated plenum cable applications. Tris-2-ethylhexyl phosphate shows good compatibility with PVC and also imparts good low temperature performance in addition to good fire retardancy.

2-Ethyhexyl diphenyl phosphate has widespread use in flexible PVC applications because of its combination of properties of plasticizing efficiency, low temperature performance, migration resistance, and fire retardancy.

Sebacate and Azelate Esters

Esters produced from 2-ethylhexanol and higher alcohols with linear aliphatic acids are used in some demanding flexible PVC applications where superior low temperature performance is required. Di-2-ethylhexyl sebacate (DOS) and di-2-ethylhexyl azelate (DOZ) are the commonly used members of this group. They offer superior low temperature performance but poorer compatibility, and command a significant premium. Their usage is generally limited to extremely demanding low temperature flexibility specifications, eg, underground jacketing cable in arctic environments.

Polymeric Plasticizers

Polymeric or polyester plasticizers are a class offering very good characteristics of low volatility, solvent, oil, stain, fat, and migration resistance to plasticized PVC. Polymerics usually are high molecular weight, linear, saturated, terminated polyesters of adipic, azelaic, or glutaric acids and propylene or butylene glycols. In most cases, termination is done by monohydric alcohols or monocarboxylic fatty acids. Polymerics have one of the following structures:

$$T_1\text{-}[G\text{-}A]_n\text{-}G\text{-}T_1 \qquad T_2\text{-}[A\text{-}G]_n\text{-}T_2$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$
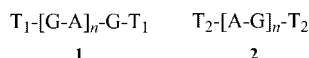
where A is a dibasic acid, G a glycol, T_1, a fatty acid, T_2 a monohydric alcohol, and n the number of repeating units.

When polycondensation is carried out with a stoichiometric excess of acid (**1**), the carboxylic end groups are esterified with monoalcohols whereas with excess diol (**2**), the terminal hydroxy groups react with acetic acid or longer chain monocarboxylic acid. The polycondensation reaction yields a broad molecular weight distribution.

Choice of acid, glycol, and terminators is very important since the total architecture of the molecule is critical to achieve good compatibility with PVC because of the high molecular weight of the polyester. Because of their high molecular weight, polymeric plasticizers need to be heated up prior to dry blending and require a higher process temperature.

Because of lower efficiency than a monomeric plasticizer and higher costs, polymerics are used frequently in combination with phthalates to improve migration resistance and oil extraction characteristics over the phthalate system. Upholstery and aircraft seating subject to extraction by body or hair oil are examples of useful applications. Refrigerator gasketing, electrical tape, decals, and oil-resistant electrical wire use high levels of polymerics frequently as the sole plasticizer (5).

Polyester plasticizers range in viscosity from 900 to 300,000 m Pa·s (cP), as shown in Table 2. They can be classified as low, medium, and high viscosity products. As the viscosity increases the extraction resistance improves and the plasticizing efficiency decreases.

The chemical nature of the polymeric plasticizer can be used to classify them in relation to end-product performance. Table 2 shows that the acid component, diol component, and end groups as well as the molecular weight determine the performance properties.

Secondary Plasticizers

Also known as extenders, secondary plasticizers continue to play a significant role in flexible PVC formulations. They do not impart flexibility to the PVC resin alone, but when combined with a primary plasticizer act in such a way as to add flexibility and other properties to the final product (6). The majority of secondary plasticizers

Table 2. Polyester (Polymeric) Plasticizers: Composition, Properties, and Applications

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, >10,000 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

in use are chlorinated paraffins, which are hydrocarbons chlorinated to a level of 30–70%. For a given hydrocarbon chain, viscosity increases with chlorine content, as does the fire retardancy imparted to the formulation. These materials aid fire retardancy because of their chlorine content. Chlorinated paraffins of the same chlorine content may have different volatilities and viscosities if they are based on different hydrocarbon chains.

Phthalate-chlorinated paraffin compatibility decreases as the molecular mass of the phthalate and the plasticizer content of the PVC formulation increase. Usually the chlorinated paraffin portion of the total plasticizer should not exceed 15%. Many compatibility graphs are available in the literature (7).

Other materials that are often referred to as secondary plasticizers include materials such as epoxidized soybean oil (ESO), epoxidized linseed oil (ELO), and epoxidized tallate oil (ETO). These act as secondary stabilizers because of their epoxy content by removing the HCl from the degrading polymer. The ETO provides the best low temperature properties of the epoxidized oils.

Plasticized Polymers: The Dominance of PVC

Over 90% of the plasticizer volume is used by the PVC industry. The reason for such high usage with PVC is that the benefits imparted by the plasticization of PVC are far greater than those imparted to other polymers. PVC is the only polymer able to accept and retain large concentrations of plasticizer. This is due in part to a morphological form comprising highly amorphous, semicrystalline, and highly crystalline regions. Without the wide range of additives available, eg, plasticizers, stabilizers, fillers, lubricants, and pigments, PVC would be of little use. The development of PVC as a commodity polymer is fundamentally linked to the development of its additives.

Different types of PVC exist on the market. The two principal types are suspension and paste PVC; the latter includes the majority of emulsions and dispersion PVC polymers. The plasticizer applications technologies associated with these two forms are distinctly different and are discussed separately. Details of the polymerization techniques giving rise to these two distinct polymer types can be found in many review articles (8) (see VINYL CHLORIDE POLYMERS).

Applications Technology

Suspension PVC.   These polymers are produced by suspending vinyl chloride in water and polymerizing this monomer using a monomer-soluble 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 3.

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

Table 3. 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

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, injection molding, and calendering to fuse the PVC and produce the end product.

The dry blend can also be extruded and the extrudate pelletized 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 (9). Microsuspension produces very fine particles of monomer to ensure that small particle sizes of polymer are produced. In emulsion or dispersion polymerization 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 of the plastisol. It is common to encounter formulations with two or three different plasticizers.

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 homogeniety. 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.
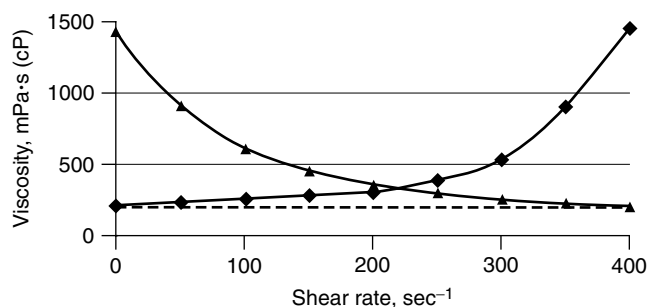
Fig. 1. Rheological behavior. - - - Newtonian; ━━ dilatent; ━▲━ pseudoplastic.

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. 1).

Effect of Plasticizer Choice on the Properties of Flexible PVC

A change in plasticizer affects the properties of a flexible PVC article. Certain properties are more important for some applications than others and some plasticizers find more extensive use in some application areas than others. The PVC technologist must ascertain the most important properties for an application and then make the correct choice of plasticizer. The two structural parameters that affect plasticizer performance are chain length or molecular weight and linearity.

In general, as the ester chain length increases, the following performance changes occur: solvation power decreases, efficiency decreases, volatility decreases, low temperature flex improves, low temperature brittleness improves, and compatibility decreases.

A comparison of linear vs branched chains show the following:

(1) Linear chains have a faster dry blend time.
(2) Branched chains have a faster fusion time.
(3) Branched chains are more compatible.
(4) Linear chains have better low temperature brittleness and flexibility.
(5) Linear chains are more efficient.
(6) Linear chains are less volatile.
(7) Branched chains have better electrical properties.
(8) Linear chains exhibit better uv stability and long-term permanence.
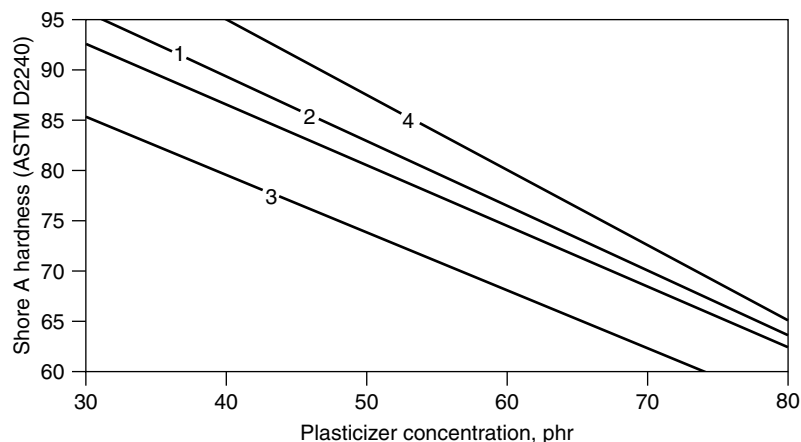(9) Linear chains provide higher thermal stability.

Fig. 2. 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 C_9 phthalate.)

Plasticizer Efficiency. This is a measure of the concentration of plasticizer required to impart a specified softness to PVC or shore hardness (Fig. 2). 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 (10). 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 (Fig. 3). Plasticizer volatilization, both from the finished article during use at elevated temperatures (eg, in electrical cable insulation) and also during processing [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 the plasticizer in use is entering 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
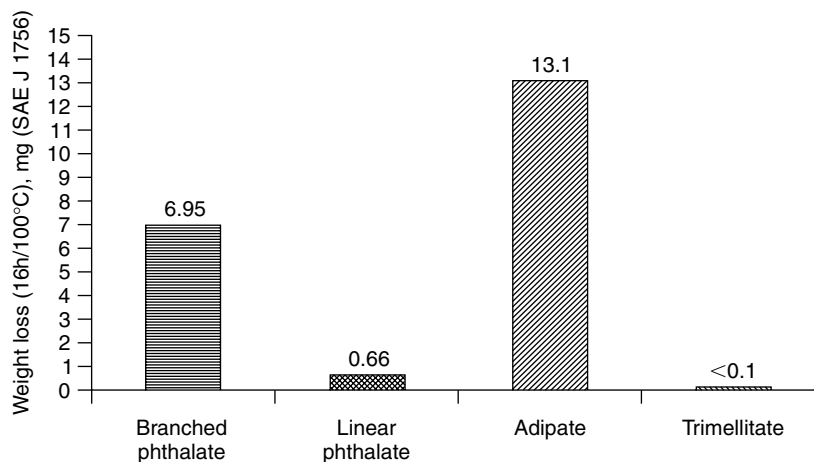
Fig. 3. Volatile loss of plasticizers from flexible PVC (Shore A80).

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 (Fig. 4).

Processing Properties. The dry blend and fusion characteristics of an FPVC are related to the molecular weight and degree of branching of the
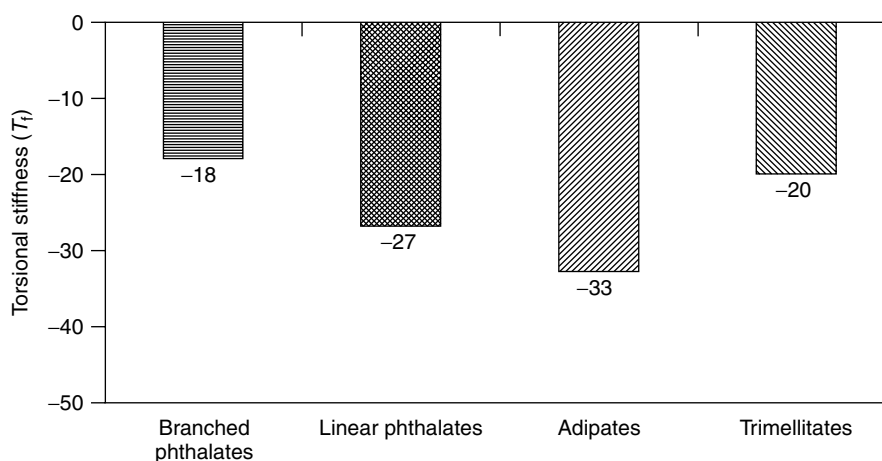

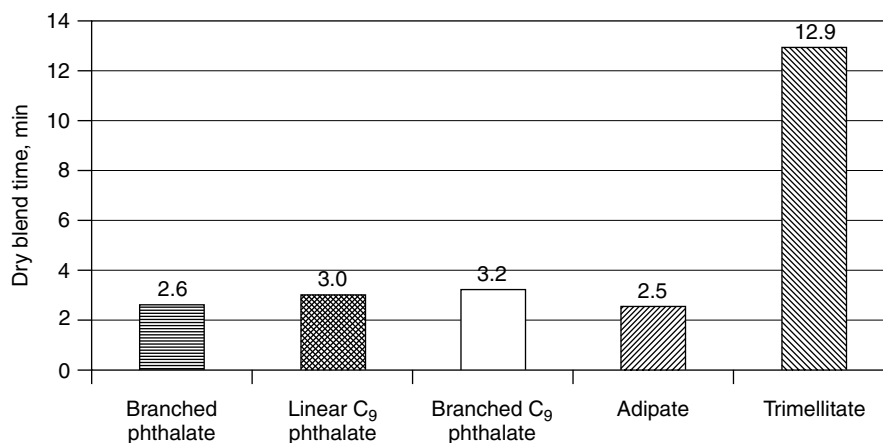**Fig. 4.** Low temperature flexibility of plasticized PVC.

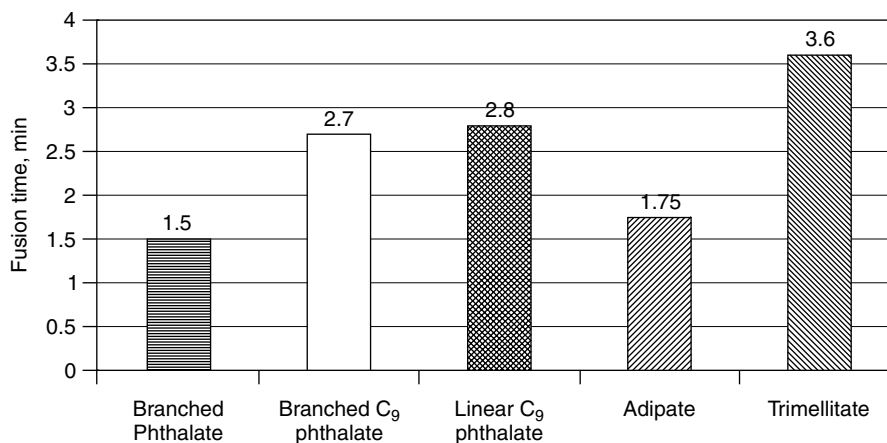**Fig. 5.**   Dry blend time of plasticized PVC.

Fig. 6.   Fusion time of plasticized PVC. Jacket temperature 96°C; rotor speed 63 rpm.

plasticizer (Fig. 5). In general, the shorter the chain length and the more linear the plasticizer, the shorter the dry blend time.

The fusion characteristics are a measure of the ability of a plasticizer to fuse with the polymer and develop maximum mechanical properties (Fig. 6). 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.
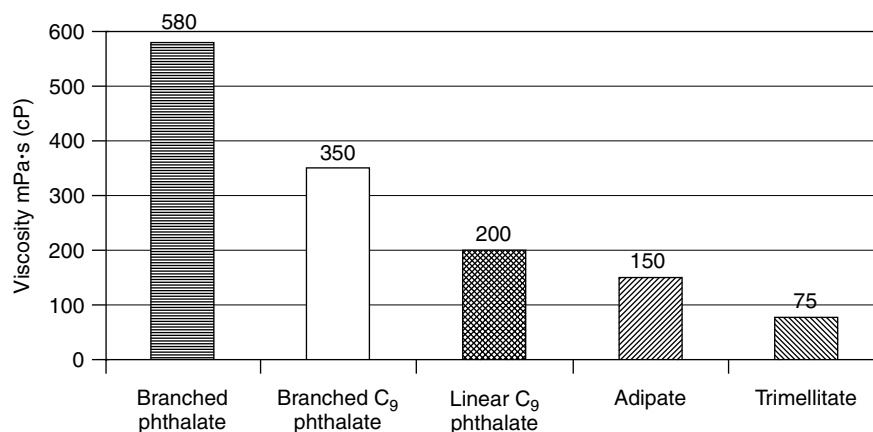
Fig. 7. Storage stability of plastisols (change in viscosity after 30 days).

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 (Fig. 7). 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 (Fig. 8). The rate of migration depends not only on the plasticizer but also on the nature of the contact material.

Plasticizer 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.
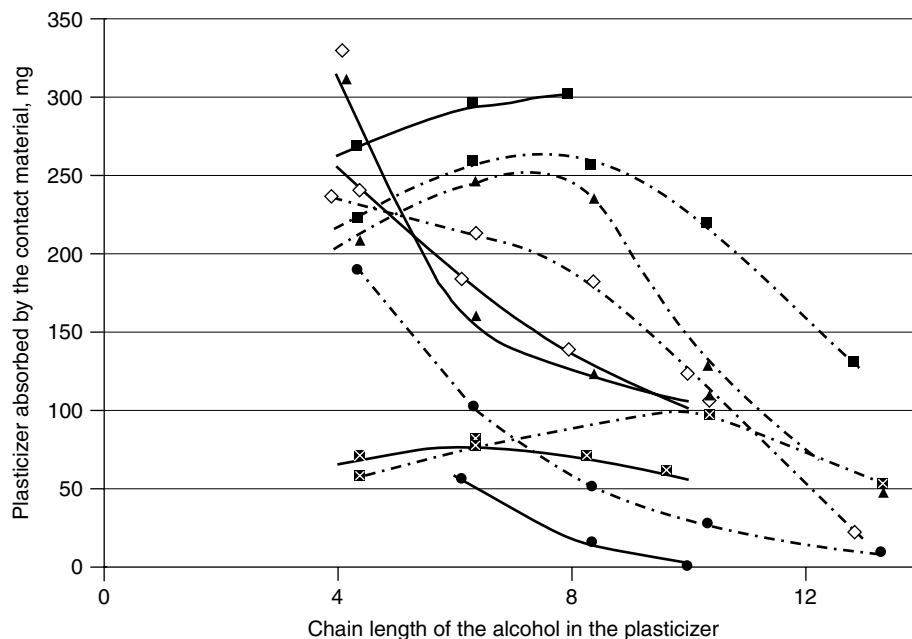
Fig. 8. Plasticizer absorption by contact material in relation to chain length of the alcohol in the plasticizer. Solid lines indicate linear alcohol and dashed lines indicate branched alochol. ──◇── Vinoflex® 507 rigid PVC; ──■── Polystyrol® 475 K impact polystyrene; ──▲── Terluran® 877 T (ABS); ──▲── Luran® 368 R (SAN); ──⊠── Lupolen® 6011 L (HDPE); ─·◇·─ Vinoflex® 507 rigid PVC; ─·■·─ Polystyrol® 475 K impact polystyrene; ─·▲·─ Terluran® 877 T (ABS); ─·▲·─ Luran® 368 R (SAN); ⊠ Lupolen® 6011 L (HDPE);

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 (Fig. 9). 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.
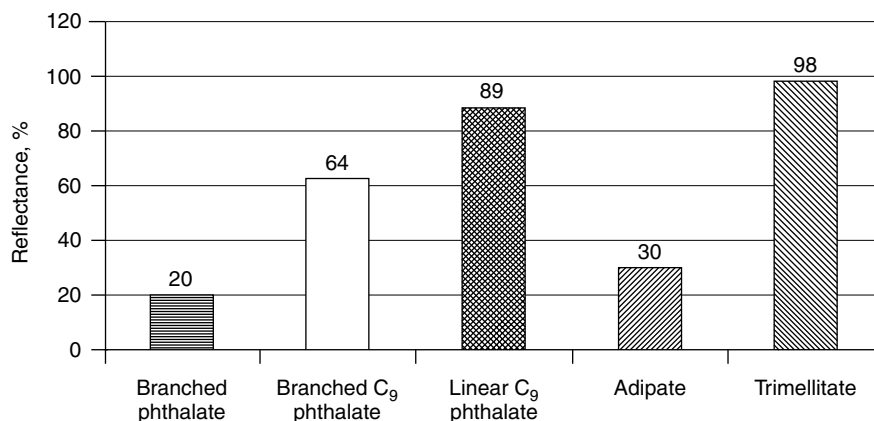
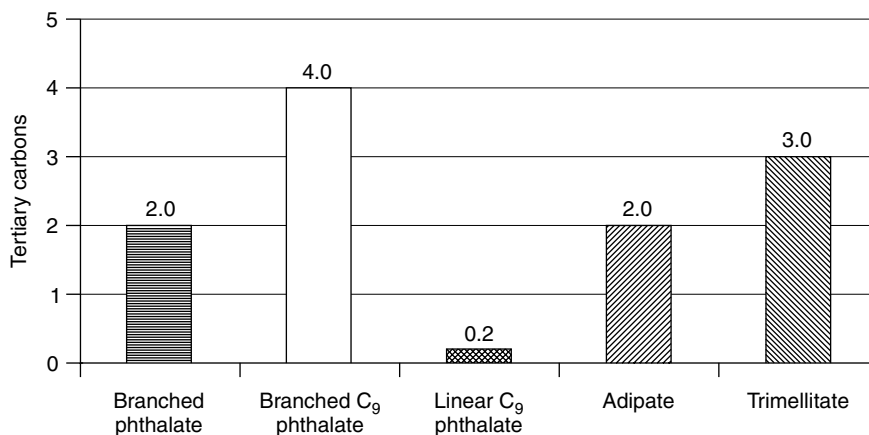**Fig. 9.**   Fogging of plasticized PVC for 3 h at 100°C (SAE J1756).

Fig. 10.   Effect of branching on tertiary carbons.

Tertiary carbon sites on the plasticizer are weak spots where heat or light can initiate radical formation, which leads to degradation of the FPVC (Fig. 10). The higher the number of tertiary carbons the greater the probability for degradation and limited outdoor life.

Overall Assessment of Properties.   Table 4 shows the effect for each criterion of increasing plasticizer concentration, increasing the size of the plasticizer molecule, increasing the linearity of the plasticizer molecule, and changing the acid constituent of the ester. There is no perfect plasticizer for every application. Choice depends on the performance requirements for the end use application and economics.

The Plasticization of Polymers Other Than PVC

The plasticization of PVC accounts for the majority of plasticizer use. However, a significant amount of plasticizers are used in non-PVC polymers. Although PVC

Table 4. Structure: Property Relationships of Plasticizers[a]

Property, at equal softness	Increased concentration	Increased size	Increased linearity	Acid[b] used Acid[b] used
Higher efficiency	–	P	I	Ph = Ad > Tr
Thermal resistance	P	I	I	Tr > Ph > Ad
Low temperature	I	I	I	Ad > Ph = Tr
Fusion	(I)	P	(P)	Ph > Ad ≥ Tr
Plastisol				
Viscosity	I	(I)	I	Ad > Ph
Aging	–	I	(I)	Ad > Ph
Migration/extraction	P	I	I	Tr > Ph > Ad
Fogging	P	I	I	Tr > Ph > Ad
Long-term permanence	–	P	I	Ph > Tr > Ad

[a]I = improved performance; P = poorer performance; ( ), marginal performance.
[b]Ph = phthalate; Ad = adipate; Tr = trimellitate.

stands alone in its ability to accept and retain large quantities of commercial plasticizer, effective plasticization of other resins may be possible if certain conditions specific to the polymer of interest are met.

The first factor to be considered when looking at the plasticization of a polymer is the need. Even though some polymers may be compatible with large concentrations of plasticizer, the resultant softening benefits may be of little use. Other factors are short- and long-term compatibility.

For a plasticizer to enter a polymer structure the polymer should be highly amorphous. 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 the suppression of crystallization in the polymer, but if crystallization subsequently occurs, the plasticizer exudes. For highly crystalline resins such as nylon, the small amounts of plasticizer allowable can change the nature of the small amorphous regions with a consequent overall change in properties.

Acrylic Polymers.   Although considerable information on the plasticization of acrylic resins is scattered throughout journal and patent literature, the subject is complicated by the fact that the acrylic resins constitute a large family of polymers rather than a single polymeric species. A 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 (see ACRYLIC ESTER POLYMERS; METHACRYLIC ESTER POLYMERS).

Plasticizers are used with acrylics to produce tough flexible coatings. Compatabilities with common plasticizers are up to 10 wt% although with low molecular weight plasticizers, it can be higher. Plasticizers for acrylics include most of the common esters. There has been interest in the development of acrylic plastisols similar to PVC plastisols. Clearly, the same aspects of both plastisol viscosity and viscosity stability are important. Patents appear in the literature indicating that the number of available plasticizers that show both good compatibility with acrylic resins and satisfactory long-term plastisol stability may be fewer than those showing equivalent properties with dispersion PVC resins.

Patents have appeared which show the formulations containing PMMA emulsion polymer and PMMA suspension polymer combined with butyl benzyl phthalate and octyl benzyl phthalate. When replacing PVC applications the use of phosphate plasticizers may be required to give equivalent fire retardance.

Nylon. The high degree of crystallinity in nylon 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. These plasticizers help improve the processing of the nylon.

Poly(ethylene terephthalate). Poly(ethylene terephthalate) (PET) is a crystalline material and hence difficult to plasticize. Since PET is used as high strength film and textile fiber, plasticization is not usually required. Plasticizers may be used in small amounts as processing aids and external lubricants.

The main area of interest for plasticizers in PET is in the area of dyeing. Because of its lack of hydrogen bonds, PET is relatively difficult to dye. Plasticizers used in this process can increase the speed and intensity of the dyeing process. The compounds used, however, tend to be of low molecular weight since high volatility is required to enable rapid removal of plasticizer from the product (see POLYESTERS, THERMOPLASTIC).

Polyolefins. Interest has been shown in the plasticization of polyolefins but plasticizer use generally results in a reduction of physical properties, and compatibility can be achieved only up to 2 wt%. Most polyolefins give adequate physical properties without plasticization.

Polystyrene. Polystyrene shows compatibility with common plasticizers but is usually internally flexibilized with butadiene rubber. Small amounts of plasticizer are used to increase the flexibility further.

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

Rubbers. Heavy petroleum oils, coal tars, and other predominantly hydrocarbon products have been used in rubber processing and formulations for many years. Esters such as DOA, DOP, and DOS, can be used with latex rubber, nitrile rubber, and chloroprene to reduce the T_g. The level of plasticizer is usually around 10–15 phr.

Economic Aspects

Worldwide consumption of plasticizers is estimated at 4.9×10^6 t (Fig. 11; Table 5) (11).

The distribution of plasticizers into various applications is shown in Figure 12.

Health and Safety Aspects

Numerous toxicological studies have been conducted on a variety of plasticizers. Because DEHP is the most widely used plasticizer and is a well-defined single

Table 5. North American Plasticizer Market[a]

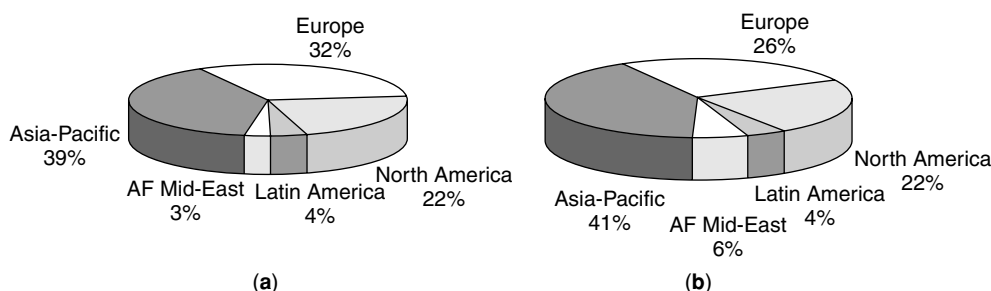| Plasticizer	Market share, %
Overall market	
C_8 phthalates	20
C_9 and C_{10} phthalates	35
C_4 phthalates	1
Linear phthalates	28
Other specialties	16
Specialty market	
Epoxies[b]	19
Adipates	31
Phosphates	9
BBP	13
Polymerics	9
Trimellitates	14
Other	5

[a]Approximate split by grade types.
[b]ESO, etc.

Fig. 11.   Worldwide plasticizer production (**a**) and consumption (**b**). ■ is Africa and the Middle Eastern countries.

substance, it is the plasticizer that has been most thoroughly investigated in terms of its toxicology. There are more than 1000 scientific publications on the toxicology and environmental effects of DEHP (12).

Acute Toxicity.   This studies the effect of the plasticizer on the species, usually a rodent, using a high dose where only a single or a few doses are given. Plasticizers posses a low acute toxicity with an LD_{50} greater than 2000 mg/kg body weight for oral route of exposure. Animal tests have indicated that plasticizers do not irritate the skin or eyes and are nonsensitizing.

Chronic Toxicity.   Various animal species have undergone repeated oral exposure to phthalates for periods up to two years. Tumors were found in rodents at a dose level higher than what humans are exposed to. In mechanistic studies these tumors were found to be specific to rodents and therefore the effect is not relevant for humans. At lower dose levels, still many times higher than what humans are exposed to, no tumors are present. In these mechanistic studies phthalates were not genotoxic. Both *in vivo* and *in vitro* studies did not indicate
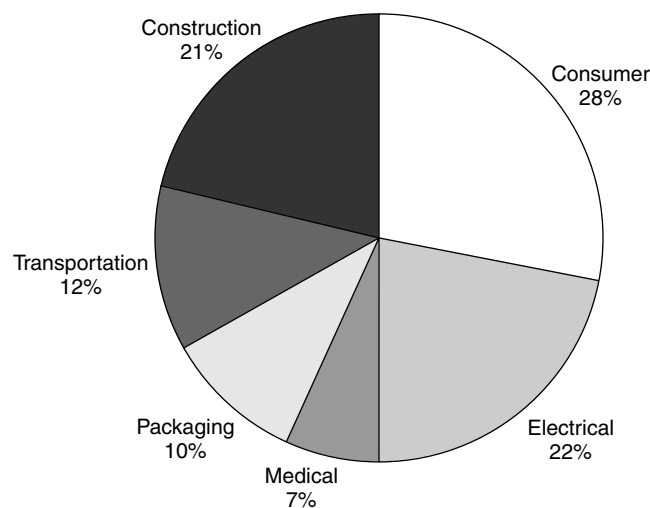
Fig. 12. Plasticizer market breakdown in North America.

any mutagenic potential. The DNA binding studies were also negative. These studies also showed that phthalates are weak peroxisome proliferators; however, peroxisome proliferation is species specific to rodents. Peroxisome proliferation was not evident in monkey and marmoset studies. Hypolipidemic drugs administered to rodents and humans cause peroxisome proliferation in the rodent but not in the human. The International Agency for Research on Cancer (IARC), a World Health Organization agency, has downgraded DEHP to category 3. DEHP is not classifiable as to its carcinogenicity to humans. The Canadian government has classified DEHP in Group IV—unlikely to be a carcinogen to humans.

Endocrine Modulation.   Some scientists claim that chemicals in the environment may adversely affect the body's endocrine system and hormones. In studying phthalates, researchers looked at their ability to mimic the female hormone estrogen. The majority of the *in vitro* (test tube) and all the *in vivo* studies indicate that phthalates do not cause estrogenic effects. Although the mechanism is unknown, recent studies show that phthalates do not bind to the androgen receptor. Additional studies are under way to investigate whether phthalates produce other hormonal changes.

Developmental and Reprotoxicity.   Some of the phthalates have shown reproductive effects in rodents at high dose levels. The relevance to humans is in question as primates appear resistant to the reproductive effects seen in rodents when tested with DEHP or DINP for 13 weeks at 2500 mg/kg/day (13).

Comparing estimates of the average human daily lifetime exposure to DEHP (0.3–6 μg/kg/day) to the level at which no effects are observed in rats indicates a margin of safety of 10,000 mg/kg/day for humans.

The Effect of Plasticizers on the Environment.   Approximately 5 million tons of plasticizer is used annually in the world (14). Over 90% of the worldwide consumption is used to make FPVC, and 95% of these PVC plasticizers are

phthalate esters. Relatively few plasticizers are used in sufficient quantity to pose an environmental impact. For plasticizer grade esters phthalates are photodegradable, biodegradable, and are not bioaccumulative. They do not pose a hazard within their solubility parameter.

Phthalates can be emitted to the environment during their production, transportation, compounding and processing, life cycle, and disposal.

Because of the effect of uv degradation and microbial attack, a significant proportion of the emissions from the flexible PVC consists of plasticizer degradation products. In these instances, therefore, the level of plasticizers appearing in the environment will be significantly less than indicated by the plasticizer loss data.

Phthalate plasticizers are produced by esterification of phthalic anhydride in closed systems and so losses to the atmosphere are minimal. Inquiries of all the principal plasticizer producers indicate a maximum total emission of 0.02–0.1%, ninety percent of which is to the water compartment. This level is expected to decrease because of improvements in plant water treatment facilities.

The road, rail, and marine transport of phthalates is carried out by international companies with sophisticated tank cleaning facilities. Wash waters from these modern facilities are passed through a series of separators to remove any residual plasticizer, which is then incinerated. It is estimated that, as a result of cleaning and spillages, the maximum emission to the environment is 0.01%.

Process operations often do not involve direct use or contact with process water. Based on the manufacturing technology applied, aqueous emissions are expected to be minimal. During the production of FPVC products, plasticizers may be exposed for up to several minutes at temperatures of $\sim 180°$C. The loss of plasticizer by evaporation and degradation can be significant.

Air extracted from spread coating ovens contains typically 500 mg/m^3 plasticizer, which is present mostly as a condensate since the saturation concentration of common plasticizers in air is low. In those installations with filtration equipment, the average phthalate concentration in the air is reduced from 500 mg/m^3 to below 20 mg/m^3. The use of incineration equipment to clean the exhaust air reduces the residual phthalate concentration to practically zero. The use of filters and incinerators on calendering and spread coating plants is steadily increasing due primarily to the need to reduce emissions of solvents and other volatile organic compounds to the atmosphere.

Knowledge of the quantity of plasticizer used in each application together with the level of exhaust air treatment allows estimation of the level of plasticizer lost to atmosphere during these processes to be between 0.007 and 0.68%, with an average of 0.11%.

Emissions During Interior End Use.   The majority of flexible PVC is used indoors in applications such as flooring, wall covering, upholstery, and wire and cable. Environ Corp. developed a model that attempts to quantify the plasticizer losses that occur in a typical room. Using theoretical and semiexperimental approaches they have arrived at an emission rate at 25°C of 2.3×10^{-4} mg/s/m^2. Using this emission rate with data on the annual production of PVC flooring, wall covering, etc, and estimates of their lifetimes, the plasticizer losses from all indoor flexible PVC articles can be calculated.

Emissions During Exterior End Use.   When flexible PVC is used in exterior applications, plasticizer loss may occur due to a number of processes which include evaporation, microbial attack, hydrolysis, degradation, exudation, and extraction. The data from FPVC roofing has been used to estimate the plasticizer losses from all outdoor applications at 0.7–1%. This estimate may be too high. Much of this extracted plasticizer does not end up in the environment because considerable degradation takes place during the extraction process.

Emissions During Disposal and Incineration.   The increasing use of modern incinerators to dispose of domestic waste results in complete combustion of plasticizers to carbon dioxide and water. The main route by which organic components are removed from a landfill is by ingress of water, extraction, and subsequent loss of water from the site to the environment. There are approximately 2000 active landfill sites with an annual combined water ingress of $40 \times 106 \, \text{m}^3$. The solubility of the most common plasticizer, DEHP, in water is difficult to measure. The true solubility is considered to be around 50 μg/L, but various values are given in the literature. Assuming a worst case solubility of 1 ppm, then the maximum quantity of plasticizer extracted in the United Kingdom is 0.005%. A maximum of 0.02% plasticizer could be emitted to the environment from landfills in Western Europe. To obtain a more precise estimate of the situation, 25 effluent water samples from a variety of types of landfills have been analyzed. The highest concentration of DEHP detected was 30 parts per billion. If the highest figure is used instead of the assumed 1 ppm then the quantity from the whole of Europe becomes 0.0006%. In conclusion, the DEHP estimated emission factors for industrial point sources are as follows: air, 0.05–0.5 wt%; surface water, 0.001–0.01 wt%; soil, 0.001–0.01 wt%. Lower molecular weight phthalates would be greater and higher molecular weight phthalates would be less.

Storage and Handling

PVC plasticizers are viscous liquids with high boiling points and a very low vapor pressure. Their flash points are all well over 100°C so they are not classified as a flammable liquid. They are thermally stable and are practically insoluble in water. They have an indefinite shelf life in a sealed container. They can be stored safely in carbon steel storage tanks or drums for extended periods of time.

Tanks may be installed in a vertical or horizontal position. The vertical position is preferred to minimize air contact with the plasticizer and for drainage. The bottom of the tank should be inclined at 2–5% in the direction of the outlet valve. Underground storage tanks are not recommended. Besides carbon steel, storage tanks are made of stainless steel, aluminum alloy (AIMg$_3$), fiberglass reinforced plastic, and high density polyethylene.

The containment basin and walls should be constructed of concrete and be large enough to contain the tank's entire contents. If a basin serves more than one tank, its capacity must be sufficient to contain 110% of the largest tank plus the maximum rainfall in a 24-h period. Most plasticizers do not require heated

storage facilities although a heated plasticizer will flow more easily and have a faster dry blend time. Diundecyl phthalate and some polymeric plasticizers should be stored indoors or in a heated storage tank because of their higher pour point and crystallization.

All plasticizers should be filtered prior to compounding to prevent contamination of the FPVC and damage to the process equipment. For handling plasticizers personnel should wear neoprene gloves, chemical goggles, chemical splash suits, and boots. Spills should be contained, solidified, and placed in a suitable container for disposal as per federal, state, and local regulations. Waste disposal is by incineration or burial in a licensed facility. Plasticizers should not be discharged into waterways or sewer systems without proper authority as per federal, state, and local regulations.

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