# PVC Handbook

## Charles E. Wilkes, Charles A. Daniels, James W. Summers

Leseprobe 1

Weitere Informationen oder Bestellungen unter
http://www.hanser.de/3-446-22714-8 sowie im Buchhandel

# 5 Plasticizers

Leonard G. Krauskopf, Allen Godwin

## 5.1 Introduction

In 1951, the International Union of Pure and Applied Chemistry (IUPAC) developed a universally accepted definition for a plasticizer as a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product.

In 2003, the worldwide market for plasticizers was more than 4.6 million metric tonnes (10 billion pounds), with approximately 90% applied as plasticizers for PVC. In North America, plasticizer consumption was about one million metric tonnes (2.2 billion pounds), with ExxonMobil Chemical, BASF, Sunoco, and Eastman Chemical Company as the major producers. The plasticizer market in Europe is about 1.3 million metric tonnes (2.8 billion pounds), with the three largest producers being ExxonMobil Chemical, Oxeno, and BASF. The region of the world with the largest plasticizer production is the Far East, with approximately 2.2 million metric tonnes (5 billion pounds) produced annually. There are numerous plasticizer producers in that region, the major producers being Nan Ya Plastics, Union Petrochemical Corp., Dahin Co., Aekyung Industrial Co, and LG Chemical.

Throughout the period from 1970 to 1995, the worldwide plasticizer markets grew at rates above the various GNPs; however this trend has started to decrease in North America and in Europe. In recent years, the average growth rate in those regions has ranged between 2 and 3%, with projected growth rates of only 1–2%. The Far East is not only the largest market for plasticizers but continues to show the highest growth rates, with the Chinese plasticizer market reported to have grown in excess of 12% in 2002. This rapid growth in China has also contributed to the decline in growth rates in many other parts of the world, as Chinese imports have displaced locally produced materials.

## 5.2 Historical Developments

Several authors have documented the historical developments of plasticizers and their use in PVC. Sears and Darby [1] provide an extensive review, including citations of the use of water and other liquids as "quasi-plasticizers" in non-polymeric materials. The use of plasticizers in PVC and other polymers originated as extensions from low volatility solvents. Weinberg [2]

points out that Waldo Semon, of B. F. Goodrich, originated the use of plasticized PVC using plastisols (dispersion of PVC particles in plasticizers). Semon's objective was to apply corrosion-resistant linings to metal storage tanks, which he accomplished via fused plastisol coatings on wire mesh secured to tank interiors. Krauskopf [3] reviewed plasticizers used in polymers, beginning with the use of camphor in nitrocellulose (1868) by the Hyatt brothers and up to Gresham's patented use of DOP (di-2-ethylhexyl phthalate) in PVC [4] in the early 1940s. The use of DOP prevailed as the preferred general-purpose plasticizer for PVC until the late 1970s. In 1968, more than 550 different materials were listed as commercial plasticizers, available from over 75 suppliers in the USA [5].

Changes in costs and availability of raw materials that serve as plasticizer feedstock have caused a significant reduction in the number of plasticizer suppliers and plasticizer products in use. Although there are still approximately 70 different plasticizers available, about 80% of the worldwide consumption is comprised of three plasticizers, di-2-ethylhexyl phthalate (DOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP).

## 5.3    Mechanisms of Plasticization

For a plasticizer to be effective, it must be thoroughly mixed and incorporated into the PVC polymer matrix. This is typically obtained by heating and mixing until either the resin dissolves in the plasticizer or the plasticizer dissolves in the resin. The plasticized material is then molded or shaped into the useful product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting mechanical and physical properties of the flexible product.

Several theories have been developed to account for the observed characteristics of the plasticization process. A significant review of the theoretical treatment of plasticization is described by Sears and Darby [6]. In this treatment, plasticization is described by three primary theories, with some modifications.

According to the *Lubricating Theory* of plasticization, as the system is heated, the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions (van der Waals' forces). Here, the plasticizer molecules act as shields to reduce polymer-polymer interactive forces and prevent the formation of a rigid network. This lowers the PVC $T_g$ and allows the polymer chains to move rapidly, resulting in increased flexibility, softness, and elongation.

The *Gel Theory* considers the plasticized polymer to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak secondary bonding forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

*Free Volume* is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has its molecules packed closely but is not perfectly packed.

The free volume is low and the molecules cannot move past each other very easily. This makes the polymer rigid and hard. When the polymer is heated to above the glass transition temperature, $T_g$, the thermal energy and molecular vibrations create additional free volume which allows the polymer molecules to move past each other rapidly. This has the effect of making the polymer system more flexible and rubbery. Free volume can be increased through modifying the polymer backbone, such as by adding more side chains or end groups. When small molecules such as plasticizers are added, this also lowers the $T_g$ by separating the PVC molecules, adding free volume and making the PVC soft and rubbery. Molecules of PVC can then rapidly move past each other. If the plasticizer uniformly went into the PVC, it would behave similarly to an uncured rubber, with lots of creep and high compression set. For example, uncured tires do not hold their shape; they require a crosslinking cure to give them dimensional stability. Likewise, a thermoplastic elastomer such as PVC requires physical crosslinks which are meltable to make them thermoplastic. These meltable crosslinks are the PVC crystallites which give PVC a physical cure. Therefore, the plasticizer must not be a powerful solvent for all the PVC parts, but must be selective in enterring the amorphous PVC part and must not enter and destroy the crystalline part of PVC.

The mechanistic explanation of plasticization considers the interactions of the plasticizer with the PVC resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the PVC resin molecules but are free to self-associate and to associate with the polymer molecules at certain sites such as amorphous sites. As these interactions are weak, there is a dynamic exchange process whereby, as one plasticizer molecule becomes attached at a site or center, it is readily dislodged and replaced by another. Different plasticizers yield different plasticization effects because of the differences in the strengths of the plasticizer-polymer and plasticizer-plasticizer interactions. At low plasticizer levels, the plasticizer-PVC interactions are the dominant interactions, while at high plasticizer concentrations plasticizer-plasticizer interactions can become more significant. This can explain the observation of "anti plasticization", wherein low plasticizer levels (< 15 phr) increase rigidity in PVC, as measured by modulus, tensile strength, elongation and low temperature properties.

For a plasticizer to be effective and useful in PVC, it must contain two types of structural components, polar and apolar. The polar portion of the molecule must be able to bind reversibly with the PVC polymer, thus softening the PVC, while the non-polar portion of the molecule allows the PVC interaction to be controlled so it is not so powerful a solvator as to destroy the PVC crystallinity. It also adds free volume, contributes shielding effects, and provides lubricity. Examples of polar components would be the carbonyl group of carboxylic ester functionality or, to a lesser extent, an aromatic ring; the non-polar portion could be the aliphatic side chain of an ester. The balance between the polar and non-polar portions of the molecule is critical to control its solubilizing effect; if a plasticizer is too polar, it can destroy PVC crystallites; if it is too non-polar, compatibility problems can arise. Useful tools in estimating plasticizer compatibility are the Apolar/Polar Ratio method developed by Van Veersen and Meulenberg [7] and the solubility parameter methods [8–11].

## 5.4    Types of Plasticizers

Plasticization is achieved by incorporating a plasticizer into the PVC matrix through mixing and heat. Plasticizers may be classified as either monomeric or polymeric plasticizers, depending on their synthesis steps, which relates in part to their molecular weight. It is preferred to categorize plasticizers on the basis of their chemical structure and associated performance when employed in PVC.

The IUPAC definition of a plasticizer is entirely focused on performance characteristics when combined with a polymer; there is no implication of chemical structure or physical properties of the plasticizer *per se.* Early technical publications, therefore, presented rather vague categorizations based on observed performance properties. Attempts to correlate neat plasticizer properties with performance characteristics were unsuccessful; generalizations became possible only after development of large, coherent databases of properties measured on flexible PVC as a function of a broad range of plasticizer levels (i.e., 20–90 phr) for many commercial and experimental plasticizers [12]. The key performance properties are influenced by plasticizer level (phr) as well as the chemical type. In addition, variations in isomeric structure and homologues within any given chemical family contribute performance variations that have been measured in flexible PVC compositions. Table 5.1 shows the major chemical families of PVC plasticizers vs. key performance criteria.

An orderly comparison of plasticizers is facilitated by separating all plasticizers types into three subgroups relating to their performance characteristics in PVC:

- General Purpose (GP): plasticizers providing the desired flexibility to PVC along with an overall balance of optimum properties at the lowest cost. These are dialkyl phthalates ranging from diisoheptyl (DIHP) to diisodecyl (DIDP), along with low cost oils called "extenders".

- Performance Plasticizers (PP): contribute secondary performance properties desired in flexible PVC beyond the GP type, while imposing somewhat higher costs. Table 5.1 identifies these key performance criteria as "Strong solvaters", "Low temperature" and "Low volatility". These include specific phthalates and other types of plasticizers. Strong solvaters have higher polarity and/or aromaticity. Conversely, low temperature types, such as aliphatic dibasic esters, are less solvating and have higher diffusivity. Low volatility requires high molecular weight plasticizers, such as trimellitates and polyesters (polymeric).

- Specialty Plasticizers (SP): provide properties beyond those typically associated with flexible PVC designed for general purpose or specialty characteristics. These exceptional characteristics are typically a function of specific chemical plasticizer families and may vary as a function of isomeric structure and/or homologues. Such properties are shown in Table 5.1 as "Low diffusivity", "Stability", and "Flame resistance". Few phthalates meet these special requirements. Polyester plasticizers provide low volatility and low diffusivity, along with low smoke (in the absence of aromaticity) under fire conditions. Epoxy plasticizers provide adjuvant thermal stability to PVC; phosphates and halogenated plasticizers provide fire retardant properties. Specialty plasticizers impose even higher costs than PP grade plasticizers.

**Table 5.1** Plasticizer Family/Performance Grid

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

X = Primary performance function
√ = Secondary performance function

Table 5.1 indicates the primary performance characteristics associated with each chemical family by "X", while "√" denotes secondary functions associated with products in that class of plasticizers. Formulating refinements in plasticizer performance and cost constitute the selection of preferred isomers and homologues of any given chemical family, or combinations thereof. Phthalates are the most widely used class of plasticizers in PVC. As shown, they contribute the most complete array of required performance properties in flexible PVC. In addition, their cost and availability supports their preference. While historically DOP – di(2-ethylhexyl) – phthalate has been the product of choice, the current market for GP plasticizers includes dialkyl phthalates that are slightly different homologues of DOP, such as diisoheptyl ($C_7$), diisooctyl ($C_8$), diisononyl ($C_9$) and diisodecyl ($C_{10}$) phthalates; their combined usage totals more than 80% of the worldwide plasticizer market. Note that the family of phthalate plasticizers show an offering in all of the performance categories, as indicated by the "√". Performance comparisons of these materials are reviewed in Sections 5.5 through 5.9.

- Phthalate esters: prepared by the esterification of two moles of a monohydric alcohol with one mole of phthalic anhydride. 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 $C_4$ to $C_{13}$ alcohols. Phthalate esters prepared from alcohols below $C_4$ are too volatile, while phthalate esters prepared from alcohols greater than $C_{13}$ 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 (DOP), which is prepared from 2-ethyl hexanol, establishes the standard against which other plasticizers may be compared.
- Extenders: shown in the general purpose plasticizer category because they are most commonly employed with phthalates to reduce costs in general purpose flexible PVC.

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 are not widely used in the U.S., 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.

"Performance Plasticizers" have three subgroups:

- "PP-SS", strong solvator;
- "PP-LT", low temperature, and
- "PP-LV", low volatility.

In addition to selected phthalate candidates, other chemical structures contribute desired performance attributes.

"PP-SS"s, strong solvaters, are a result of increased 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.

"PP-LT"s 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 $C_{18}$ and $C_{26}$. 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.

Plasticizer structural relationships with low temperature performance will be reviewed in Sections 5.5 through 5.9.

"PP-LV"s 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 DIDP (446). 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 DTDP (530). High molecular weight phthalates having low volatility and compatibility with PVC include DIUP, UDP, DTDP, 911P, and DUP, all shown in Table 5.2. Two chemical families are noted for their use as low volatility plasticizers – trimellitates and polyesters (also referred to as polymerics).

**Table 5.2** Plasticizer Acronyms, Chemical Compositions, and Substitution Factors

| Acronym | Chemical structure | Molecular weight | Subst.* factor |
|---|---|---|---|
| *Phthalates* | | | |
| BBP | butyl, benzyl | ca. 312 | 0.94 |
| BOP | butyl, 2-ethylhexyl | ca. 365 | 0.94 |
| DHP | di(isohexyl) | 334 | 0.96 |
| DIHP | di(isoheptyl) | 362 | 0.97 |
| DOP | di(2-ethylhexyl) | 390 | 1.00 |
| DIOP | di(isooctyl) | 390 | 1.01 |
| DCP | di(2-normal-octyl) (aka capryl) | 390 | NA |
| DINP | di(isononyl) | 418 | 1.06 |
| DIDP | di(isodecyl) | 446 | 1.10 |
| DIUP | di(isoundecyl) | 474 | 1.16 |
| UDP | di(iso $C_{11}$, $C_{12}$, $C_{13}$) | ca. 502 | 1.21 |
| DTDP | di(isotridecyl) | 530 | 1.27 |
| *Linear phthalates* | | | |
| DBP | di(*n*-butyl) | 278 | 0.86 |
| 79P | di(linear $C_7$, $C_9$) | ca. 390 | 1.00 |
| NHDP(610P) | di(*n*-$C_6$, $C_8$, $C_{10}$) | ca. 418 | 0.99 |
| DNNP | di(*n*-nonyl) | 418 | 0.94 |
| L9P | di(linear nonyl) | 418 | 0.99 |
| 7911P | di(linear $C_7$, $C_9$, $C_{11}$) | ca. 418 | 1.00 |
| 911P | di(linear $C_9$, $C_{11}$) | ca. 446 | 1.05 |
| DUP | di(linear $C_{11}$) | 474 | 1.14 |
| *Trimellitates* | | | |
| NODTM | tri(*n*-$C_8$, $C_{10}$) | ca. 592 | 1.12 |
| TOTM | tri(2-ethylhexyl) | 546 | 1.17 |
| TIOTM | tri(isooctyl) | 546 | 1.19 |
| TINTM | tri(isononyl) | 588 | 1.27 |
| *Adipates* | | | |
| 79A | di(linear $C_7$, $C_9$) | ca. 370 | 0.90 |
| DOA | di(2-ethylhexyl) | 370 | 0.93 |
| DIOA | di(isooctyl) | 370 | 0.94 |
| DINA | di(isononyl) | 398 | 0.98 |

**Table 5.2**     (continued)

| Acronym | Chemical structure | Molecular weight | Subst.* factor |
|---------|--------------------|--------------------|----------------|
| *Phosphates* | | | |
| DDP | isodecyl, diphenyl | 390 | 0.96 |
| TOF | tri(2-ethylhexyl) | 435 | 1.00 |
| TCP | tricresyl | 368 | 1.31 |
| *Epoxides* | | | |
| OET | 2-ethylhexyl epoxy tallate | ca.   410 | 0.96 |
| ESO | epoxidized soybean oil | ca. 1,000 | 1.10 |
| *Others* | | | |
| DOTP | di(2-ethylhexyl)terephthalate | 390 | 1.03 |
| DINCH | di(isononyl) cyclohexane-1,2-dicarboxylate | 422 | NA |

\*     Substitution factor = PHR required for 80A Durometer hardness at room temperature vs. required DOP level (52.9 phr).

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

"Specialty Plasticizers" are also divided into three subgroups:
• "SP-LD" for low diffusion;
• "SP-Stab" for stabilizing function, and
• "SP-FR" for fire resistance in PVC.

Low diffusivity is contributed by high molecular weight and highly branched isomeric structures. Diisodecyl phthalate (DIDP) and diisotridecyl phthalate (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.

*Polymeric* plasticizers are typically polyesters, with a molecular weight range from 1,000 to 8,000. Polyethylene copolymers (EVA's, VAE's, etc.) and terpolymers can range up to > 500,000. 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 polymerics reportedly have a proven history of providing good weathering resistance [13].

Interestingly, the trimellitate plasticizers demonstrate improved resistance to diffusivity-controlled losses only under certain conditions. Trimellitates in combination with polyester plasticizers control migration from PVC refrigerator gaskets, which can cause crazing of the ABS door liner. However, trimellitates fail to provide reduction of plasticizer diffusivity under oil immersion tests.

*Pentaerythritol* esters are a type of "miscellaneous" plasticizers that impart both low volatility and diffusivity. 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.

*Epoxy plasticizers* 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 [14]. 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. 1,000, 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. A commercial curiosity of the "epoxidized phthalate-type" structure was found to contribute beneficially to thermal stability, while otherwise imparting the expected properties of the dialkyl phthalate counterpart [15].

Flame resistant plasticizers include halogenated (preferably brominated) phthalates and the phosphate family. Brominated phthalate esters are produced by the esterification of tetra-bromophthalic anhydride with various alcohols, most typically 2-ethylhexanol. *Phosphate* plasticizers which may be considered as "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. Trialkyl phosphates (like TOF) are less efficient in fire resistant properties. Commercial phosphate plasticizers use combinations of aryl and $C_8$ and $C_{10}$ 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 [16]. Phosphate plasticizers may be combined with phthalates to reduce formulating costs.

Miscellaneous plasticizers include "phthalate-like" esters, benzoates, sulfonates, pentaerythritol esters, citrates, and similar materials.

*"Phthalate-like"* esters include DOIP [di (2-ethylhexyl) *meta* (called "iso") phthalate], and DOTP [di (2-ethylhexyl) *para* (called "tere") phthalate], which are isomeric structures of DOP. DOTP is commercially available at similar costs to DOP; Section 5.8 reviews the performance

characteristics of DOIP and DOTP. Hexamoll® DINCH is di (isononyl) cyclohexane-1,2-di-carboxylate [17], the hydrogenated product of the corresponding di $C_9$ phthalate ester(DINP). As indicated [15], its performance characteristics in PVC are expected to be similar to the phthalate counterpart, except for having less solvency for PVC. DINCH has recently been introduced by BASF as a candidate for applications with sensitivity for peculiar health and environmental concerns. These sensitivities are also addressed with the recent introduction of a novel triester plasticizer completely devoid of carbon ring configurations; it is claimed for use in medical applications and "low smoke" grade PVC electrical insulations [18].

*Benzoates* are the esterification products of benzoic acid and selected glycols, usually diols. Preferred glycols are dipropylene glycol and butane diols. One commonly used benzoate is dipropylene glycol dibenzoate (DPGDP, commercially Benzoflex® 9-88). Its preferred use is in PVC flooring products, owing to its strong solvating strength, and it reportedly controls plasticizer bleeding into asphalt adhesives. Benzoflex® 1046 is a mixed ester of benzoate ester of Texanol®. Texanol is an "ester-ol" resulting from the Aldol and Tischenko condensation reactions of three moles of isobutyraldehyde. Esterification with benzoic acid yields the mixed ester. Its preferred use is in vinyl sheet flooring, where the benzoate enhances processing, while the low molecular weight contributes a hardened, stain resistant surface, due to volatilization.

*Sulfonates* also exhibit strong solvency for PVC. Mesamoll® is a product of Bayer; it is described as the phenyl cresyl esters of pentadecyl sulfonic acid. It is reportedly resistant to hydrolyses and diffusion controlled plasticizer losses.

*Citrates* are promoted for plasticized PVC applications facing exceptional toxicological and/or environmental constraints. However, neat citric acid does not meet PVC compatibility requirements. Therefore, citrate plasticizers are tetraesters, resulting from the reaction of one mole of an organic acid (with the single alcohol group) and three moles of alcohol, which esterify the three acid groups.

## 5.5    Plasticizer Performance

The previous section summarized key plasticizer families and associated performance characteristics. Within each family, there are a variety of isomeric structures and homologues that contribute measurable variations in performance. The phthalate family includes a great variety of isomers and homologues that are useful as plasticizers for PVC. This, then, is an appropriate plasticizer family for the evaluation of the effects of chemical structures in PVC. Generalizations derived from phthalate structures appear to translate into other chemical families as well. Performance plasticizers (PP) contributing low volatility include those having molecular weights greater than that of DIDP (446) and those of less branching (oxidative resistance). Linear alkyl structures contribute low temperature properties as well as lower volatility. All aliphatic dibasic esters, such as the adipates, contribute exceptional low temperature properties. The chemical structures that contribute improved low temperature properties typically impart lower plastisol viscosities, due to their own lower viscosity; likewise, their reduced tendency for solvation of PVC resin contributes to improved viscosity stability

under storage conditions. On the negative side, the low temperature type plasticizers impair compatibility in PVC and diffusion-controlled plasticizer loss in end use applications. Octyl epoxy tallate (OET) and tri(2-ethylhexyl) phosphate demonstrate performance characteristics similar to those of low temperature plasticizers.

Performance plasticizers having strong solvating characteristics include phthalates having higher polarity and aromaticity. These structural features also contribute increased volatility due to smaller non-polar tails. Non-phthalate plasticizers having strong solvency are highly aromatic (benzoates, TCP) or other more polar structures such as sulfonates.

Epoxy plasticizers contribute the unique feature of enhancing thermal stability, and also contribute plasticization properties consistent with their molecular structure. That is, epoxidized oils (about 1,000 molecular weight) enhance low volatility, while monoester OET enhances low temperature performance.

Disciplined studies of carefully controlled model formulations, sample preparation, and conditioning have shown little correlation between neat plasticizer properties and their performance in PVC [19–22].

Key physical properties appear to correlate with plasticizer performance in PVC only when the comparisons are restricted to homologues of a given chemical family. Further correlation of physical properties of the neat plasticizer with performance in PVC is confounding; a summary of key physical and performance properties of plasticizers for PVC verifies the point [15].

The only mild chemical interaction between plasticizers and PVC polymers allows for the calculation of predicted specific gravity of the plasticized PVC compositions. Yet this chemical association precludes quantitative prediction of plasticizer losses due to volatilization (i.e., using vapor pressure), or diffusion-controlled migration [19, 23–25]. Oxidative or hydrolytic degradation, on the other hand, have the opposite effect when attempting to predict plasticizer transience from PVC.

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 5.3.

This example shows typical properties for general purpose PVC containing DINP levels ranging from zero (rigid vinyl) to about 600 phr (parts per hundred resin, by weight). The average consumption of plasticizers in flexible PVC stands at 50 phr. Useful commercial products typically range from about 20 to 100 phr; fishing lures, at about 600 phr, are an exceptional product.

Reliable generalizations of plasticizer structure/performance relationships require extensive evaluations using disciplined model formulations, raw materials, sample preparation, and conditioning in the measurement and cataloging of the data. Such procedures have been described [12]. Other publications have utilized these data to provide analyses and comparisons of various commercial and experimental plasticizers [15, 23, 26–28]. The translation of this basic information to specific property requirements of flexible PVC products is enhanced by an awareness of some generalizations relevant to properties influenced by plasticizer chemical structure as well as level (phr) in the PVC, as follows:

**Table 5.3**   Typical Properties of General Purpose Vinyl Plastic Products

|  | Rigid | Semirigid | Flexible | 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[a] at 23 °C<br>MPa<br>psi | <br>> 900<br>> 130,000 | <br>69<br>10,000 | <br>12<br>1,700 | <br>3.4<br>500 | <br>–<br>– |
| Tensile strength[b]<br>MPa<br>psi | <br>> 41<br>> 6,000 | <br>31<br>4,500 | <br>21<br>3,100 | <br>14<br>2,000 | <br>–<br>– |
| Elongation (%)[b] | < 15 | 225 | 295 | 400 | – |
| Brittleness[c]<br>°C<br>°F | <br>> 23<br>> 73 | <br>−16<br>+3 | <br>−32<br>−26 | <br>−47<br>−53 | <br>–<br>– |
| *Examples* | Bottles, pipe, siding, records | Shades, shoe heels, thin films, produce wrap | Wall-covering, book-binders, upholstery, garden hose | Boots, gloves, water beds | Fishing lures |

[a]   ASTM D 747
[b]   ASTM D 882
[c]   ASTM D 746

*Source: Krauskopf, L. G., in Encyclopedia of PVC, 2nd ed., Nass, N. L. and Heiberger, C. A. (Eds.), Marcel Dekker (1988), p. 149 (reprinted with permission)*

- *Hardness* (softness) is significantly influenced by plasticizer level, as well as type of plasticizer, which controls plasticizer "efficiency".

- *Tensile strength* and *ultimate elongation* (% extension at failure) are influenced by plasticizer level, but these properties are not significantly altered as function of plasticizer type 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). Modulus values vary significantly as a function of plasticizer level, and are somewhat influenced by plasticizer type (efficiency) when measured at room temperature and formulated to specified hardness. The three different techniques for determination of modulus at room temperature result in significantly different absolute values, due to variations in test methodology forces of extension, compression, and shear.

- *Low temperature* properties, both low temperature modulus and brittleness, are significantly influenced by plasticizer level (phr) and type. Low temperature modulus values are determined by ASTM D 1043 (Clash-Berg, $T_f$), while brittleness temperature is determined by ASTM D 746 ($T_B$).

NOTE: Reliable measurements of failure properties require that test specimens be completely free of surface imperfections (nicks/cuts), completely fused and conditioned at room temperature (ASTM conditions preferred) for at least 24 hours following preparation of specimens.

Variations in isomeric structure are primarily imparted by the nature of the alkyl moiety. These configurations are a function of the starting materials and processes used to produce the plasticizer-grade alcohols. Plasticizers made with more linear (less branched) molecular structures are more efficient, and impart improved low temperature properties and volatilization and oxidative resistance [29, 30]. Krauskopf [31] differentiated plasticizer performance effects as a function of five different degrees of branching using commercial grade di($C_8$),di($C_9$), and di($C_{10}$) phthalates; these were grouped as:

- *Normal:* 100% unbranched; primarily an academic product, except for a limited amount of commercial products based on mixtures of normal $C_6$, $C_8$, and $C_{10}$ alcohols.
- *Linear:* a mixture of normal and monomethyl branched alcohols. These "linear" alcohols are produced by the hydroformylation (Oxo process) of normal alpha olefins. The resultant alcohol is approximately a 70/30 molar ratio of normal/2-methyl branched isomers.
- *Slightly branched (SLBR):* primarily a mixture of monomethyl and dimethyl branched alcohols. Commercially, the "slightly branched" alcohols are the hydroformylation products of octenes that are dimerized normal butenes. The resultant alcohol (nonanol) is a random mixture of monomethyl octanols and dimethyl heptanols.
- *Moderately branched (MODBR):* primarily dimethyl or monoethyl (i.e., 2-ethylhexyl) branched; these serve as the major type in "General Purpose" plasticizer category. "Moderately branched" nonanol is the hydroformylation product of mixed olefins generated by the dimerization of a mixture of propylene and normal butene feeds. The resultant olefin is a mixture of hexenes, heptenes, and octenes, which are separated by distillation. The octenes are hydroformylated to give nonanol mixtures primarily composed of dimethyl substituted $C_7$ backbones.
- *Highly branched (HIBR):* triple methyl branched; a specific product available in Europe. The "highly branched" nonanols are the hydroformylation product of trimethyl branched pentenes which are a product of dimerized isobutene; the resultant alcohol is primarily 3,5,5-trimethyl hexanol. These are notably susceptible to oxidative attack, while showing increased resistance to diffusivity.

These variations in degrees of branching demonstrate measurable effects on PVC properties with respect to plasticizing efficiency, low temperature properties, diffusivity, volatility, and stability to thermal and oxidative degradation. The normal $C_9$ phthalate has a substitution factor (S.F.) of 0.94, while the plasticizing efficiency of the "linear" nonyl phthalate is equivalent to that of DOP (S.F. = 1.00). When compared at equivalent hardness in PVC, the "linear" phthalate is only slightly deficient to the normal nonyl phthalate with respect to low temperature

properties and volatility. The "moderately branched" (MODBR) DINP shows less plasticizing efficiency (S.F. = 1.06) and a deficiency in low temperature properties and volatility vs. the normal nonyl phthalate. Compared to DOP performance at specified room temperature hardness, the DINP (MODBR) provides equivalent low temperature properties with significantly lower volatility. The performance of the "slightly branched" (SLBR) DINP is essentially equivalent to a 50/50 mixture of di (normal nonyl) phthalate and moderately branched DINP (MODBR).

Wadey studied a series of designed isomeric variations of DINP and the effects on plasticizer performance in PVC [30]. The conclusions are consistent with the generalizations cited above.

## 5.6    Plasticizer Efficiency

Plasticizer "efficiency" may be quantified as a function of PVC Durometer hardness. Similar comparisons may be made for other mechanical properties, but hardness test reliability and the common practice of a designated room temperature hardness value supports its use to quantify plasticizing efficiency. Figure 5.1 graphically portrays quantitative determination of plasticizer efficiency, expressed as "Substitution Factor" (SF); in this example, the hardness values are compared for DINP (MOD-BR) to DOP [di-2-ethylhexyl phthalate] plasticized PVC.
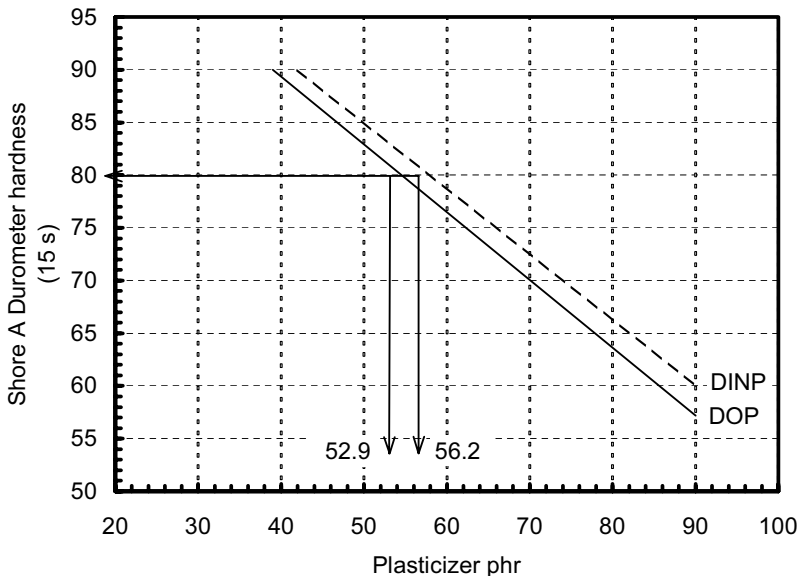


**Figure 5.1**    Durometer A hardness of DINP vs. DOP
*(Source: Krauskopf, L. G., in Handbook of PVC Formulating, Wickson, E. J. (Ed.) (1993) Wiley, New York, p. 171, courtesy John Wiley, reprinted with permission)*

It is shown that 80 Durometer A hardness is provided by 52.9 phr DOP, while 56.2 phr DINP is required to provide the same hardness. Thus, the substitution factor (SF) for DINP vs. DOP is 1.06, as shown in Equation 5.1:

$$\text{Substitution Factor (SF)} = \left( \frac{\text{phr plasticizer at Durometer 80}}{\text{phr DOP at Durometer 80}} \right) = \left( \frac{56.2 \text{ phr DINP}}{52.9} \right) \quad (5.1)$$

The "SF" indicates that DINP-MODBR is 6% less efficient than the plasticizing efficiency of DOP. In other words, DINP needs to be added at a level 6% higher than the DOP level, in order to achieve the same hardness or softness. It has been found that this ratio (substitution factor) is consistent over plasticizer levels ranging from about 20 to 90 phr. The question of acceptability, then, rests on comparative formulating costs and other critical properties provided at the specified room temperature hardness. In general, it is found that when compared at equivalent hardness, the DINP-MODBR plasticized PVC will have preferred low temperature properties as well as significantly less plasticizer loss due to volatilization and diffusivity. Most commercial grades, and many experimental plasticizers, have been evaluated in PVC over a wide range of levels (phr). The disciplined cataloguing of the performance properties allows for easy comparisons of cost effective formulating options at specified hardness values as well as at specified plasticizer levels. A computer program includes optimizations as a function of filler content as well as plasticizer selection and predicted properties in PVC [22]. Table 5.2 lists relative plasticizing efficiency values determined for commercial grade plasticizers, along with acronyms, chemical compositions, and molecular weights.

## 5.7    Low Temperature

Tables 5.4 and 5.5 show low temperature flex ($T_f$) and brittleness ($T_B$) for PVC using different plasticizers. Table 5.4 compares low temperature properties when formulated to equivalent room temperature hardness (80A Durometer); Table 5.5 shows low temperature properties at equivalent plasticizer levels (50 phr, by weight), in a recipe commonly used for "screening" plasticizer performance.

It is shown that for given alkyl structures, the trimellitate family provides similar or only slightly improved low temperature properties vs. the phthalate counterparts, because of the need for higher plasticizer levels to provide the target room temperature hardness, due to the lower plasticizing efficiency of trimellitates versus phthalates. Adipate plasticizers, on the other hand, impart significantly improved low temperature properties (by about –25 to –35 °C) versus their phthalate counterparts, in spite of the fact that they are more efficient (substitution factors of < 1.00) in providing target room temperature hardness. The more linear alkyl structures in the plasticizer contribute improved low temperature properties (by about –5 to –7 °C) vs. the branched isomers. They also have lower substitution factors (higher plasticizing efficiency) to meet room temperature hardness. It should be noted that end-use products require low temperature tests to be conducted on whatever form, or shape, the product has.

**Table 5.4**    Low Temperature Properties of Unfilled, General Purpose PVC, Formulated to Meet 80 A Durometer Hardness at Room Temperature

|  | $T_f$ (°C)[a] | $T_B$ (°C)[b] |
|---|---|---|
| **Phthalates** | | |
| BBP | −10.7 | −12.1 |
| BOP | −25.8 | −31.1 |
| DIHP | −24.6 | −32.9 |
| DOP | −27.7 | −34.9 |
| DIOP | −27.5 | −32.8 |
| DOTP | −31.9 | −36.5 |
| DINP | −29.2 | −35.8 |
| DIDP | −31.6 | −37.8 |
| DIUP | −32.2 | −37.8 |
| UDP | −32.8 | −41.8 |
| DTDP | −39.3 | −42.9 |
| 610P | −36.1 | −45.5 |
| 79P | −35.7 | −40.2 |
| 7911P | −34.9 | −42.2 |
| L9P | −37.4 | −44.4 |
| 911P | −39.8 | −47.6 |
| DUP | −43.0 | −53.7 |
| **Trimellitates** | | |
| TOTM | −29.4 | −39.0 |
| TIOTM | −27.5 | −37.8 |
| TINTM | −31.4 | −38.8 |
| **Adipates** | | |
| DOA | −50.9 | −61.7 |
| DIOA | −49.3 | −63.2 |
| DINA | −51.6 | −64.4 |
| 79A | −52.5 | −66.1 |

PVC formula by weight:
PVC-100, plasticizer (concentration adjusted to yield a shore A of 80),
Liquid Ba/Cd/Zn stabilizer – 2.0, stearic acid 0.25.
[a]    ASTM D1043
[b]    ASTM D746

**Table 5.5**   Low Temperature Properties of Unfilled, General Purpose PVC at 50 PHR Plasticizer

| | $T_f$ (°C)[a] | $T_B$ (°C)[b] |
|---|---|---|
| **Phthalates** | | |
| BBP | −11.0 | −12.3 |
| BOP | −26.9 | −31.9 |
| DIHP | −23.6 | −32.3 |
| DOP | −24.9 | −32.9 |
| DIOP | −23.8 | −30.0 |
| DOTP | −27.7 | −33.4 |
| DINP | −23.6 | −31.8 |
| DIDP | −23.6 | −31.8 |
| DIUP | −22.4 | −30.5 |
| UDP | −20.9 | −32.9 |
| DTDP | −24.4 | −31.5 |
| 610P | −33.5 | −43.5 |
| 79P | −32.7 | −38.0 |
| 7911P | −32.0 | −40.2 |
| L9P | −34.3 | −42.1 |
| 911P | −34.3 | −43.4 |
| DUP | −33.3 | −45.9 |
| **Trimellitates** | | |
| TOTM | −19.2 | −31.8 |
| TIOTM | −15.9 | −29.1 |
| TINTM | −17.3 | −27.9 |
| **Adipates** | | |
| DOA | −52.8 | −62.7 |
| DIOA | −49.8 | −63.5 |
| DINA | −50.5 | −63.8 |
| 79A | −55.3 | −67.6 |

PVC formula by weight:
PVC-100, plasticizer – 50
Liquid Ba/Cd/Zn stabilizer – 2.0, stearic acid 0.25.
[a]   ASTM D1043
[b]   ASTM D746

Thus, performance test results measured on finished commercial PVC plastics may be influenced by factors other than the formulating predictions. For example, incompletely fused or improperly conditioned, or otherwise damaged, specimens may experience undue failure in mechanical property testing.

Likewise, the translation of catalogued values may require experience. For example, properly prepared PVC insulation for electrical conductors typically meets low temperature mandrel bend testing at temperatures approximately –15 °C lower than the predicted brittleness ($T_B$ by ASTM D 746) values of formulated PVC.

## 5.8    Permanence (Transience) of Plasticizers

Plasticizers have a strong affinity for PVC polymers, but do not undergo a chemical reaction that causes bonding, or grafting, to the polymer. Note, however, that epoxy plasticizers are an exception, in that they undergo chemical grafting onto PVC in their role as stabilizers, replacing labile chlorides [14] in addition to their role of acid absorption. Other functional additives are known to graft and/or polymerize in the PVC matrix, but these are generally not considered as traditional "external" plasticizers. Copolymers for example, can lower PVC's $T_g$ as plasticizers do. But at the same time, any significant level of co-monomer will disrupt the syndiotactic PVC structure and disrupt the ability to form crystallites. The crystallites are the physical cross-links that hold the structure together as a thermoplastic elastomer. Thus with copolymers, creep increases, compression set increases, and long-term elasticity is lost. Thus, the plasticizers, when not grafted or copolymerized, may be separated from the PVC matrix due to extraction by solvents, oils, water, surface rubbing, volatility, migration into adjacent media, or degradation mechanisms.

Investigations of plasticizer transience found that quantitative predictions were confounded by "compatibility", which was difficult to quantify [19, 20, 24, 25]. However, Quackenboss determined that two controlling mechanisms (other than effects of degradation) are at play under conditions that contribute to loss of plasticizer. These are the rate of loss that occurs at the surface of the specimen vs. the rate at which the plasticizer diffuses to the surface; the slowest rate is the controlling factor. For example, most plasticizers have extremely low solubility in water, and therefore exhibit surface-controlled loss rates under aqueous environments. Plasticizer losses due to extraction by oily media (in which plasticizers are highly soluble) are controlled by diffusivity rates. Volatile losses of plasticizer are influenced by vapor pressure, solvency strength for the polymer and oxidative degradation, as well as the ambient airflow rate in the test chamber. It is known that test chamber atmospheres saturated with plasticizer vapor allow for reversed absorption of plasticizer into the test specimens. Polymeric plasticizers of high molecular weight ($\approx$1,000 to > 500,000) and of bulky molecular structures show excellent permanence because of low diffusivity. However, this family of plasticizers is also noted for sensitivity to hydrolytic degradation in aqueous atmospheres.

Dialkyl phthalate plasticizers range in molecular weight from 278 (dibutyl) to about 530 (ditridecyl). Commercial experience has shown that dibutyl is unacceptably volatile (except in some adhesive applications), while ditridecyl phthalate is useful for PVC applications under

high temperatures for extended periods; trimellitates and polyesters are typically even lower in volatility. Preferred "General Purpose" plasticizers range in molecular weight from 362 (DIHP) to 418 (DINP), while DOP has an intermediate molecular weight at 390. The volatility of DINP is significantly less than that of DOP, while DIHP is significantly more volatile than DOP in most applications. This characteristic often dictates the preferred choice of the general purpose plasticizer for given applications. Di(linear alkyl) phthalates impart lower volatility and improved oxidative resistance vs. their branched counterparts. All phthalate, trimellitate, and aliphatic dicarboxylic diesters show excellent resistance to hydrolytic attack under exposure to aqueous environments. Diffusion-controlled transience is poor for the aliphatic dicarboxylic diesters, but good for branched phthalates; linear dialkyl phthalates are measurably less resistant than the branched phthalates, but significantly better than the aliphatic dicarboxylic diesters. Oil extraction resistance of trialkyl trimellitates is not good compared to that of phthalates. This is apparently due to their lower plasticizing efficiency as well as to the increased proportion of alkyl moieties in the molecular structure.

Two isomers of DOP have been found to have novel resistance to migration into F2 nitrocellulose lacquer finishes [32, 33]. These are known as DOIP [di 2-ethylhexyl *meta* (called "iso") phthalate] and DOTP [di 2-ethylhexyl *para* (called "tere") phthalate].

Their overall performance in PVC Is similar to that of DOP, except for a slight indication of being less compatible. The "mar resistant" feature may also be imparted to flexible PVC by alternate practices, such as top coating technology and/or the use of polyester plasticizers. However, this novel performance trait of DOIP and DOTP remains largely a technical anomaly.

## 5.9    Solvency, Miscibility, or Compatibility

These terms are essentially interchangeable with respect to liquids and other lower molecular weight reagents added to PVC. Whether rigid or flexible, the systems behave as solid solutions, and abide by the three-dimensional solubility parameter concept of Hansen [10, 34]. Bench scale methods designed to measure the solvency, miscibility, or compatibility of plasticizers – and other reagents – in PVC are confounded by the simultaneous effect of diffusibility. This interfering mechanism is present when attempting to measure plasticizer take-up, gelation temperatures, or compatibility (phase separation). While the solubility forces are extremely small (units are $(cal/cm^3)^{1/2}$), their presence is responsible for the energy required to molecularly combine plasticizers with PVC resin (up-take or swelling) and to hold them together (compatibility for duration of the application).

A statistical analysis of independent plasticizer variables versus take-up rates in PVC [11, 35] showed the following relationships. Equation 5.2 expresses dry blend time as a function of plasticizer viscosity and specific gravity for phthalates, trimellitates, and aliphatic dicarboxylic diesters that are used as plasticizers in PVC.

Dry Blend Times @ 88 °C = 10.05 + 0.218 · (Viscosity) − 10.08 · (Specific Gravity)    (5.2)

Where:

> Dry Blend Times are minutes using ASTM D 2396, viscosity is plasticizer viscosity at 88 °C, centistokes (cS), specific gravity is specific gravity of the plasticizer at 20 °C.

That study found that the statistical confidence for evaluating plasticizer take-up is significantly improved by limiting the analyses to the eleven commercial grade phthalates tested. Equation 5.3 expresses dry blend time as a function of plasticizer viscosity (distinctly) for dialkyl phthalates:

$$\text{Dry Blend Times @ 88 °C} = -0.067 + 0.282 \cdot (\text{Viscosity}) - 0.012\,(\text{Viscosity} - 8)^2 \qquad (5.3)$$

Similar relationships were developed for gelation temperatures. Equation 5.4 shows initial gelation temperatures are a function of plasticizer molecular weight and solvency strength for dialkyl phthalates, while Equation 5.5 shows that dialkyl phthalate plasticizers influence final gelation temperature exclusively as a function of solvating strength.

$$\text{Initial Gelation Temperature} = -8.35 + 0.118 \cdot (\text{MW}) + 0.001 \cdot (\text{MW} - 450)^2 + 21.4 \cdot (\delta) \quad (5.4)$$

$$\text{Final Gelation Temperature, °C} = 71.48 + 39.30 \cdot (\delta) \qquad (5.5)$$

Where:

> Initial gelation temperature for plastisols, °C, ref. [36], final gelation temperature for plastisols, °C, ref. [36], MW is molecular weight of the plasticizer, $\delta$ is Hansen's Interaction Radius (HIR).

HIR is the distance between PVC resin and the plasticizer on Hansen's three-dimensional solubility parameter grid. Smaller values of $\delta$ indicate stronger interaction forces. The investigation that developed plastisol gelation values [36] indicated that the ultimate fusion temperature is a function of the PVC resin, to the exclusion of plasticizer solubility parameters.

## 5.10   Processability

The ease with which various processes combine the liquid plasticizer with PVC polymer is a function of the physical and chemical properties of the plasticizer as well as the polymer characteristics. The mixing, fluxing, fusing, and shaping of the vinyl involves the application of elevated temperatures, up to about 160 °C to 170 °C. Thus, plasticizer fuming (volatility) is of concern. In addition, the rheology of plastisols (dispersions of PVC in plasticizer) critically impacts the ease of shaping and controlling thickness of end products; further, initial and final gelation temperatures (influenced by plasticizer selection) influence processing of plastisols.

As shown in Section 5.9, plasticizer selection influences dry blend rates. Melt viscosity, during "hot compounding" processes, is influenced by plasticizer characteristics, including solvency

for the PVC resin. Many investigators have studied these characteristics. Commercial practice includes the use of up to 10–20% of the plasticizer system as "strong solvating" type plasticizers, such as aryl-alkyl phthalates, benzoates, sulfonates, and so forth. Volatility is typically the limiting factor on use levels of strong solvating plasticizers. Higher molecular weight plasticizers typically offset volatility while imposing constraints on ease of processing.

## 5.11    Plasticizer Markets

Plasticizers are used to produce flexible PVC products for many different end uses or market segments. Figure 5.2 depicts a worldwide analysis of plasticizer consumption by PVC market segments.

The largest market segment is film, sheeting, and coated substrates. In this segment, the majority of plasticizer consumed is for products produced in calendering operations. The primary factors in plasticizer selection are low cost and ease of processing, with DOP meeting this requirement in most parts of the world. In North America and Europe, DINP is the preferred plasticizer choice based on the above criteria and factoring in regulatory issues regarding the use of DOP. If greater permanence is required, plasticizers such as DIDP, L9P, 911P, and DUP may be used. For coated substrates prepared through a coating process, plastisol viscosity, gelation or fusion behavior, and emissions are all-important concerns. DINP is found to give a more consistent, stable viscosity than DOP while reducing emissions. For products that need a slight reduction in gelation or fusion temperature, DIHP (diisoheptyl phthalate) or BBP can be used to replace a small portion of the primary plasticizer.

Vinyl flooring is another major market for plasticized PVC. There are basically three types of products: vinyl tile, resilient vinyl sheet flooring, and vinyl backed carpeting or carpet squares. Floor tiles are comprised of about 80% calcium carbonate held together by the fused flexible PVC binder. The most commonly used plasticizers in floor tiles are DOP and DINP, while
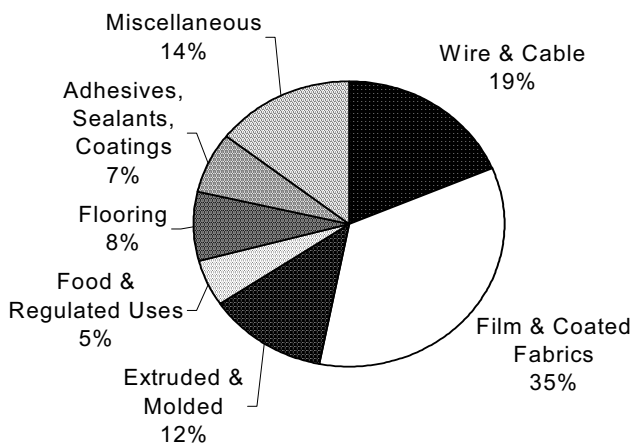


**Figure 5.2**   End use markets for plasticized PVC