Selecting Plasticizers for Polymers

Plasticizers are the most common additives used in the plastics industry. But, selecting the right plasticizer for an application has always been a daunting task. Explore various plasticization methods along with their benefits and learn how to select the right plasticizer from the main chemical classes of plasticizers: phthalates, benzoates, adipates etc. along with their current regulatory updates.

What are Plasticizers?

Plasticizers are relatively non-volatile organic substances (mainly liquids). When incorporated into a plastic or elastomer, they help improve the polymer's:

- Flexibility
- Extensibility, and
- Processability

Plasticizers **increase the flow and thermoplasticity** of a polymer by decreasing the viscosity of the polymer melt, the glass transition temperature (Tg), the melting temperature (Tm) and the elastic modulus of the finished product without altering the fundamental chemical character of the plasticized material.

Plasticizers are among the most widely used additives in the plastic industry. They are also usually cheaper than other additives used in polymer processing. Plasticizers are most often used in PVC, the third largest polymer by volume after PP and PE. In turn, PVC is used in a wide range of products. Examples include:

- **Unplasticized PVC (or rigid PVC)** is used in applications such as pipes, siding, and window profiles.
- **Plasticized PVC (or flexible PVC)** finds applications in automotive interior trim, cables, PVC films, flooring, roofing and wall coverings, etc.

Classification of Plasticizers

Plasticizers are commonly classified based on their chemical composition. It is possible to understand the influence of structural elements (e.g. different alcohols in a homologous series of phthalates, adipates, etc.) on the properties of plasticizers and their effect on base polymers.

Different plasticizers affect different physical and chemical properties of materials. Therefore, you need a particular plasticizer to change properties in a certain direction to meet requirements.

There are several general chemical families of plasticizers that are used for polymer modification. Among them, the most commonly used are:

1. **Phthalate Esters** – They are produced by esterification of phthalic anhydride or phthalic acid obtained by the oxidation of orthoxylene or naphthalene. Most commonly used phthalate plasticizers include:

a. **DEHP:** Low molecular weight ortho-phthalate. Still the world's most widely used PVC plasticizer
b. **DINP, DIDP:** High molecular weight ortho-phthalates

2. **Aliphatic dibasic acid Esters** – These include chemicals such as glutarates, adipates, azelates and sebacates. They are made from aliphatic dibasic acids such as adipic acid and alcohols.

3. **Benzoate Esters** – They are esterification products of benzoic acid and selected alcohols or diols.

4. **Trimellitate Esters** – They are produced by esterification of trimellitic anhydride (TMA) and typically C8 – C10 alcohols

5. **Polyesters** – They are formed by the reaction of many combinations of dicarboxylic acids and difunctional alcohols.

6. **Citrates** – They are tetraesters, resulting from the reaction of one mole of citric acid with three moles of alcohol. Citric acid's lone hydroxyl group is acetylated.

7. **Bio-based Plasticizers** – They are based on epoxidized soybean oil (ESBO), epoxidized linseed oil (ELO), castor oil, palm oil, other vegetable oils, starches, sugars etc.

8. **Others** – Includes Phosphates, Chlorinated Paraffins, Alkyl Sulfonic Acid Esters and more

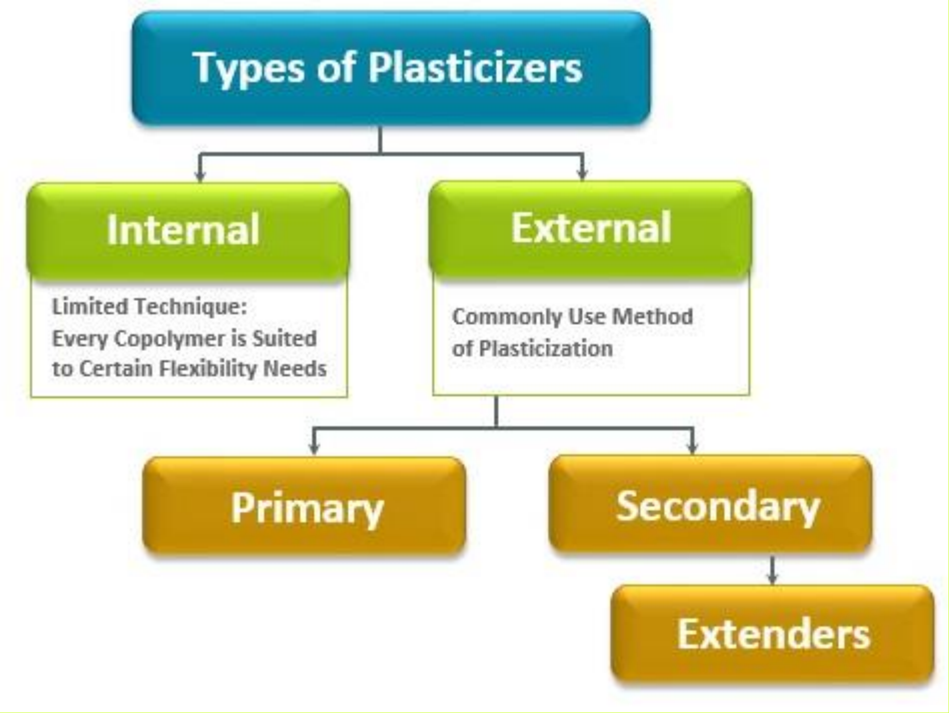
When added to polymer, these plasticizers provide several benefits as listed below.

They make a product softer, improve flexibility

- The processing becomes possible or easier
- Plasticized products do not break easily at cold temperatures

Plasticization Methods & Processing with Plasticizers

There are two main principal methods exist for plasticization - Internal Plasticization and External Plasticization.



1. **Internal Plasticization**
   A polymer can be internally plasticized by chemically modifying the polymer or monomer so that the flexibility is increased. It involves copolymerization of the monomers of the desired polymer (having high Tg) and that of the plasticizer (having low Tg) so that the plasticizer is an integral part of the polymer chain. The most widely used internal plasticizer monomers are:

- Vinyl acetate
- Vinylidene chloride

But this technique is limited: every copolymer is only suited to certain flexibility requirements

Also, the complexity of the reaction can lead to longer reaction times and increased costs. Internally plasticized materials show temperature dependence and dimensional instability at high temperatures.

2. **External Plasticization**
   This is the most commonly used method of plasticization because low-cost liquid plasticizers give the formulator freedom in developing formulations for a range of products (from semi-rigid to highly flexible depending on the quantity). The most widely used external plasticizers include esters formed from the reaction of acids or acid anhydrides with alcohols. There are two main groups of external plasticizers:

- A **primary plasticizer** enhances elongation, softness and flexibility of polymer. They are highly compatible with polymers and can be added in large quantities. For example: up to 50% of vinyl gloves are made up of plasticizers, which make the PVC flexible and soft enough to wear.

- A **secondary plasticizer** is one that typically cannot be used as the sole plasticizer in a plasticized polymer. Secondary plasticizers may have limited compatibility with the polymer and/or high volatility. They may or may not contain functional groups which allow them to solvate the polymer at processing temperatures. Secondary plasticizers are variously used for:

- Cost reduction
- Viscosity reduction
- Solvency enhancement
- Surface lubricity augmentation, and
- Low temperature property improvement

- **Extenders** are a subset of secondary plasticizers. They are commonly employed with primary plasticizers to reduce costs in general purpose flexible PVC. They are mostly low cost oils having limited compatibility in PVC. They are added to reduce cost and in some cases to improve fire resistance. Examples of extenders include naphthenic hydrocarbons, aliphatic hydrocarbons, chlorinated paraffins (fire resistance) and others.

Processing with Plasticizers

Suspension PVC (S-PVC) process is the common method to manufacture PVC:

- PVC obtained in the form of particles with size 50-200 microns
- Lower flexible PVC formula costs
- PVC particles obtained are mixed with plasticizers & can be extruded in pellets which are further used for processing via extrusion, calendaring, injection molding…
- Processing equipment is typically very expensive

Incorporation of an external plasticizer in PVC polymer enhances its flexibility. Addition of plasticizer chiefly involves five distinct steps:

- Plasticizer mixed with resin
- Plasticizer penetrates and swells the resin particles
- Polar groups in the PVC resin are freed from each other
- Plasticizer polar groups interact with the polar groups on the PVC chain
- PVC structure is re-established Upon cooling, with full retention of plasticizer

Loss of Plasticizers\ Plasticizer Exudation

The incompatibility between polymer and plasticizer can cause exudation. There are several factors which can lead to migration of plasticizer out of plastics surface (or into or onto a substrate to which it is held in intimate contact) like temperature change, humidity change, mechanical stress, weathering, etc.
Loss of plasticizer can lead to less flexibility, embrittlement, and cracking.

All About Phthalate Plasticizers & Current Regulations

Phthalates are typically produced by esterification of phthalic anhydride obtained by the oxidation of orthoxylene.

Dioctyl Terephthalate (DOTP, DEHT) Plasticizer Molecule

Phthalates appear virtually colorless with a faint odor. They have limited solubility in water but are miscible in many of the organic solvents (mineral oil etc.)

Phthalate Plasticizers Benefits & Limitations

Benefits	Limitations
They are the conventional choice as they resist extraction, evaporation and migration Phthalates offer durability, flexibility, weather resistance and are able to withstand high temperatures Phthalates are economical when compared to other plasticizers	In polymers like PVC, phthalates do not bind chemically and leach out of plastics, leading to their occurrence in the environment Some phthalate plasticizers can pose serious risks to health as they are carcinogens and/or developmental toxins Certain phthalates can accumulate at low levels in the human body

Phthalate Plasticizers Applications

Cost: Phthalates which have been used as PVC plasticizers since the earliest days of flexible PVC are both inexpensive and effective. The collapse of oil prices which began in 2015 has further reduced the price of petrochemicals, including phthalate esters. Some phthalate replacements, notably bio-based products, have seen increasing feedstock prices over this time period widening an already present cost differential.

1. **Performance:** Certain of the (currently) most widely used phthalate replacement products have processability and permanence limitations.

2. **Supply:** The worldwide plasticizer market is quite large, over 7 million tons per year. There's not yet enough manufacturing capacity to produce those volumes of phthalate replacements.

a. In electrical and electronic applications, phthalate plasticized PVC is used for insulating wires and cables.
b. Phthalate plasticizers are widely used in vinyl based building materials like floorings and wall coverings to provide them with flexibility and durability.

Phthalate Plasticizer Regulations

2001-2006 - DINP and DIDP Are Safe for Use in Current Applications – ECPI Report

The results of the risk assessments for DINP and DIDP, published in April 2006, show that these substances pose **no risk to human health** or the environment in any of their current applications.

2012 – Australia Risk Assessment Confirms DIDP & DINP Safe for Toys - NICNAS Report

In 2012, the Australian Government Department of Health and Aging found that current exposures to DINP **do not indicate a health concern** for children, even at the highest exposure levels considered.
Specifically, the report concludes: *"Current risk estimates do not indicate a health concern from exposure of children to DINP in toys and child-care articles even at the highest (reasonable worst-case) exposure scenario considered."*

There are currently no restrictions on the use of DINP in toys and child-care articles in Australia.

2013 – EC Confirms Safe Use of DINP and DIDP in all current consumer applications – EC Report

The European Commission (EC) has re-evaluated the restriction on plasticizers DINP (diisononyl phthalate) and DIDP (diisodecyl phthalate). The Commission has concluded that *"no unacceptable risk has been characterized for the uses of DINP and DIDP in articles other than toys and childcare articles which can be placed in the mouth"*.

The Commission therefore concluded that the existing restriction of DINP and DIDP in toys and childcare articles which can be placed in the mouth should be maintained. The Commission further concluded that "in the light of the absence of any further risks from the uses of DINP and DIDP, the evaluation of potential substitutes has been less pertinent".

2014 – US CHAP Lifted Ban on DIDP, DNOP and Prohibits >0.1% level of DINP in Child Care Products

U.S. Consumer Product Safety Commission (CPSC) established a Chronic Hazard Advisory Panel (CHAP) to study and review the potential adverse effects of phthalates used in children's toys and child care articles on children's health under section 108 of the Consumer Product Safety Improvement Act of 2008:

- Three types of phthalates (DEHP, DBP, BBP) are banned permanently in any amount greater than 0.1% in children's toys and certain child care articles.
- Three additional types of phthalates (DINP, DIDP, DNOP) were banned on an interim basis in any amount greater than 0.1%.

CHAP provided its report and recommended the following actions:

- Permanent ban on DBP, BBP, and DEHP remain unchanged; Additionally DIBP, DPENP, DHEXP, and DCHP at levels greater than 0.1% to be added to the existing permanently prohibited list
- Interim Ban on DINP at levels greater than 0.1% in children's toys and child care articles to be made permanent
- Current bans on DNOP and DIDP be lifted
- Use of DIOP on an interim basis until sufficient data are available to determine whether a permanent restriction is necessary
- No action on DMP, DEP, and DPHP at this time, but it did encourage appropriate agencies to gather "necessary exposure and hazard data to estimate total exposure to the phthalate alternatives and assess the potential health risks."

There were also efforts early in the Obama administration to further regulate phthalates under the authority of legislation passed in 1976, the Toxic Substances

Control Act (See TSCA sec 5b). However, this was never done.

2017 - Danish EPA Proposal on DINP

Following the fourth re-submission in two years, Danish EPA dossier proposing classification of DINP as a reproductive agent, was accepted by ECHA and the public consultation was initiated in April 2017. Though extensive prior testing, regulatory evaluations, and peer reviewed published scientific reviews the scientific data does not support this classification proposal.

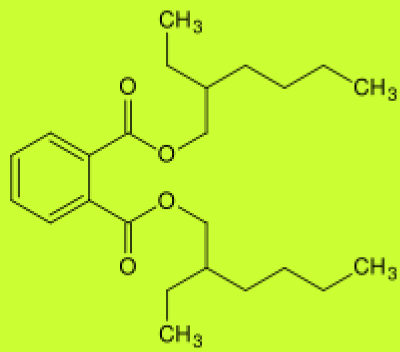
2018 - ECHA RAC Concludes DINP Requires No Classification - ECHA News

ECHA's Risk Assessment Committee (RAC) has concluded that Di-isononyl phthalate (DINP) does not warrant classification for reprotoxic effects under the EU's Classification, Labelling and Packaging (CLP) regulation.
RAC undertook a stringent hazard assessment following the rules of the CLP regulation, with the conclusion that, given the lack of evidence of adverse effects, classification is not required. Amongst prior regulatory assessments, the ECHA evaluation of new scientific evidence – endorsed by the European Commission in 2014 – concluded that *DINP can be safely used in all current applications*. All relevant data are included in the DINP REACH registration dossiers, which were updated in 2015 and 2016.

DEHP - Diethylhexyl Phthalate

Di-2-ethylhexyl-phthalate (DEHP, formula: $C_6H_4(C_8H_{17}COO)_2$) is a low molecular weight ortho-phthalate produced by esterification of phthalic anhydride with 2-ethyl-hexanol. It is non-volatile, colorless and odorless viscous liquid, soluble in oil, but not in water. Due to its low cost and generally good performance, DEHP is widely employed as a plasticizer in manufacturing articles made of PVC.

Melting point: −50°C
Boiling point: 250 - 257°C at 0.5 kPa



Structure of DEHP

DEHP offers good gelling, satisfactory electrical properties and helps to produce highly elastic compounds with reasonable cold strength. It displays fairly good flexibility at low temperatures and some resistance to high-temperature.

However, DEHP is listed by the IARC as a human carcinogen. DEHP has been implicated as a hormone mimicker and as a developmental toxin in certain studies. In the EU DEHP is considered a SVHC (substance of very high concern) under REACH legislation and cannot be used in most products. It extracts readily into non polar solvents (oils and fats in foods packed in PVC). Therefore the US Food and Drug Administration (FDA) permits use of DEHP-containing packaging only for foods that predominantly consist of water

DEHP is used in applications, such as:

- Manufacturing articles made of PVC, copolymers of vinyl chloride and vinyl acetate
- Medical devices like catheters, tubings etc.
- In developing various formulations ranging from glassy compositions to soft and highly flexible materials
- Use is decreasing due to concern about its effects on human health but DEHP is still the most widely used plasticizer in the world.

DEHP Replacement

Terephthalate esters, particularly di-2-ethylhexyl terephthalate, are the most popular replacements for DEHP. They are less compatible with PVC but their low cost and long history as commercial plasticizers are their most attractive features.

Dialkyl terephthalates with sidechains containing more than 8 carbon atoms have limited compatibility with PVC. Dialkyl terephthalates in which sidechains contain fewer than 8 carbon atoms have volatility issues. Learn about some benefits and limitations of terephthalate ester in the table below.

Cost	Low
Compatibility with the PVC polymer	Fair
Outdoor weatherability	Fair
Low temperature flexibility	Good
Plasticizer solvency	Fair to Good
Bio-based content	Typically none
Flame retardancy	Poor
High temperature service	Fair

Low plastisol viscosity	Good
Solvent extraction resistance	Poor
Hydrolysis resistance	Fair

DEHP has been progressively deselected for technical reasons such as loss of performance over time, regulation etc. It is progressively substituted by DINP (and DIDP). HMW plasticizers show a particular utility for uses requiring long term performance or durability. Processability, performance, availability and economics have made DINP a “general purpose” phthalate like DEHP and or DIDP. Therefore, DINP appears to be an alternative to most of the uses of DEHP.