The Function and Selection of Ester Plasticizers

Plasticizer basics

As defined by ASTM, a plasticizer is a substance incorporated into a plastic or elastomer to increase its flexibility, workability or distensibility.[1] In its simplest concept, it is a high-boiling organic solvent that, when added to a rigid substance, imparts flexibility. Plasticizers include a large variety of organic liquids, such as petroleum fractions, coal tar distillates, animal fats and plant extracts, and reacted products made of those materials. Ester plasticizers, the subject of this paper, are the latter. Elastomer and plastic polymers may be tough, dry or rigid materials that, for many applications, have a need for plasticizers. A plasticizer, among other contributions, will reduce the melt viscosity, lower the temperature of a second order glass transition (Tg) or lower the elastic modulus of a polymer. This paper discusses ester plasticizers, one of the more common and important plasticizer classes.

Function

Plasticizers are polymer modifiers, as are all the other ingredients included for the formation of an elastomer compound. Plasticizers may be thought of according to their function in a compound or by their type. Some of those classifications might be internal, external, chemical, physical, esters, oils, primary, secondary, etc. Internal plasticizers include flexible monomers (soft segments) incorporated regularly or irregularly between inflexible monomers (hard segments) of a polymer chain. Flexible polymers may be added to rigid polymers, for example, nitrile rubber to polyvinyl chloride (PVC), or grafted as side chains that reduce crystallinity and Tg through the reduction of intermolecular forces. External plasticizers are materials that interact physically with the elastomer but that do not chemically react with the polymer. Solvent and non-solvent are two distinct types of external plasticizers.

Common esters and polymeric polyesters are both external and physical plasticizers. Physical plasticizers may have some weak attraction to the polymer, such as through hydrogen bonding or Van der Waals forces, but, as with external plasticizers, they do not chemically react with the elastomer. An exception to this can occur under the right conditions provided one of the reactants used to make the plasticizer, after the esterification reaction, retained a reactive group. A potential problem arises here, however, as materials reacted with the polymer molecules will make the polymer molecule larger and thus less flexible. Chemical plasticizers attack, thereby reducing the molecular weight of the elastomer chain.

The bulk of this paper is about esters, which will be discussed in detail later. Oils are not a part of the products considered in this paper but include aromatic, naphthenic and paraffinic petroleum products and natural products such as castor or rapeseed oils.

Under suitable conditions, esters are solvents for amorphous polymers, that is, the polymer would eventually dissolve in the plasticizer. With crystalline or semi-crystalline polymers, some plasticizers may enter the crystalline (ordered) and the amorphous (disordered) regions.

Primary and secondary plasticizers are terms related to compatibility with polymers (compatibility is discussed later). Primary plasticizers enter the polymer systems first. Plasticizers entering the crystalline regions of crystalline or semi-crystalline polymers are referred to as primary. If the amorphous regions of those polymers are penetrated, the plasticizer may be considered a solvent type. Secondaries are plasticizers that do not penetrate the original polymer-only system and that are used as diluents for primary plasticizers.

External plasticization permits the greatest latitude in formulating for specific compound properties and may be the least expensive route for that need. In the instance of PVC, esters are quite compatible as primaries. Petroleum oils are not useful as primaries. However, by incorporating an ester as a primary, the desired properties of softness, low temperature and processing may be achieved. Then a limited amount of petroleum oil may be incorporated, and frequently is, strictly to reduce compound cost. The petroleum oil is compatible with the primary plasticizer and thus stays in the PVC compound. On the elastomer side, esters are essentially incompatible with Ethylene Propylene Diene Monomer (EPDM) polymers. However, by incorporating petroleum oil with EPDM, esters may be included in those recipes successfully. The purpose is to achieve properties the petroleum oils will not provide to that elastomer, such as original compound low temperature, which accompanies high green strength EPDM.

We have stated that plasticizers can have two distinctly different uses. Table I below shows their different functions and in general the effects as 1) process aids and 2) property modifiers.[2]

TABLE I

Physical Functions of Plasticizers
(depending upon choice of material)

as processing aids -

- Lower the processing temperature
- Increase lubricity
- Reduce mixer sticking
- Reduce mold sticking
- Increase tackiness
- Improve flow out
- Improve wetting
- Reduce nerve

as elastomer property modifiers -

- Soften the polymer
- Lower the modulus
- Lower the tensile strength
- Increase elongation
- Increase flexibility
- Lower glass transition
- Increase tear strength
- Increase the temperature range of usefulness
- Increase cohesion
- Modify frictional character
- Improve surface appearance
- Decrease static charge

Ideally, a process aid should reduce the temperature of processing without affecting the softening temperature of the final product (Figure 1.1). The softening temperature will be the upper limit of usefulness of that final product. A plasticizer as a final property modifier will ideally lower the Tg temperature or softening temperature without lowering the flow temperature (Figure 1.2). This represents a broadening of the temperature range of usefulness desired from the plasticizer. The softening temperature will now be the lower limit of usefulness of the finished product. As an example, apply that reasoning to rubber tires used in arctic regions.[3] Plasticizer added to the recipe lowers the compound Tg, providing the compound with improved low temperature for the cold climate. This allows the tire to have a colder softening temperature but does not alter the flow temperature of the compound.

Fig. 1.1 - Response to Plasticizer As Process Aid[2]

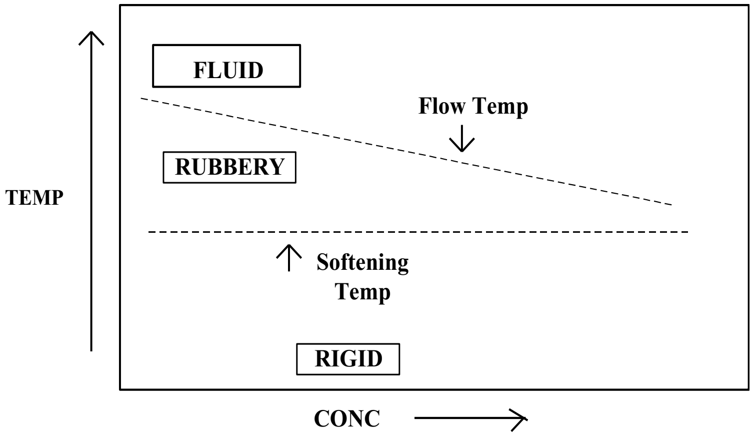
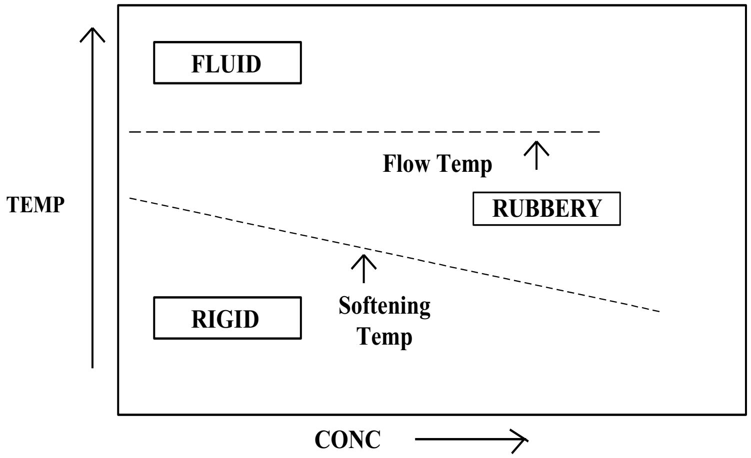


Fig. 1.2 - Response to Plasticizer for End Use[2]



Plasticizer theory

There are four theories that describe the effects of plasticizers: [4,5,6,7]

1. Lubricity theory

The lubricity theory states that a plasticizer acts as a lubricant between polymer molecules. As a polymer is flexed, it is believed their molecules glide back and forth with the plasticizer, thus providing the gliding planes. The theory assumes the polymer macromolecules have, at the most, very weak bonds away from their cross-linked sites. Figure 2 illustrates this theory.

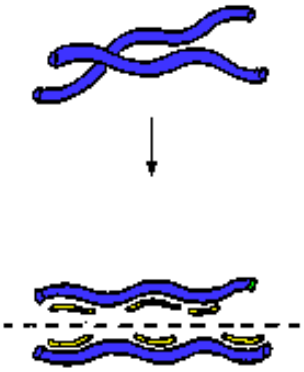


Fig. 2 Plasticizer polymer response based on lubricity theory

2. Gel theory

The gel theory of plasticization starts with a model of the polymer molecules in a three-dimensional structure. The stiffness of the polymer results from a gel of weak attachments at intervals along the polymer chains. These points of gel are close together, thus permitting little movement. Gel sites might be the result of Van der Waals forces, hydrogen bonding or crystalline structure. The gel sites can interact with the plasticizer, thus separating a gel site of the adjacent polymer chains. The plasticizer by its presence separates the polymer chains, allowing the polymer molecules to move more freely.

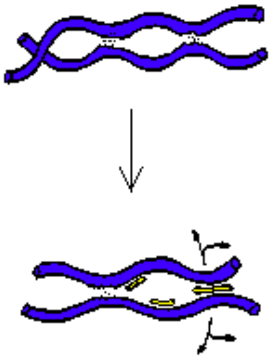


Fig. 3 Gel theory of plasticizers

3. Free volume theory

The free volume theory involves low-temperature flexibility. For any polymer, the simplest explanation may be stated as the difference between the observed volume at absolute zero and the volume measured at a selected temperature. The addition of a plasticizer to a polymer increases the free volume of the system. Likewise, free volume increases with rising temperature.

An important application of the theory to external plasticization has been to clarify the lowering of the Tg temperature of a compound by a plasticizer. Plasticizers, because of their small molecular size compared to polymers, assist with greater polymer mobility. This is attributed to increased free volume until the temperature at which the polymer–plasticizer mixture freezes. Figure 4 illustrates the free volume theory.

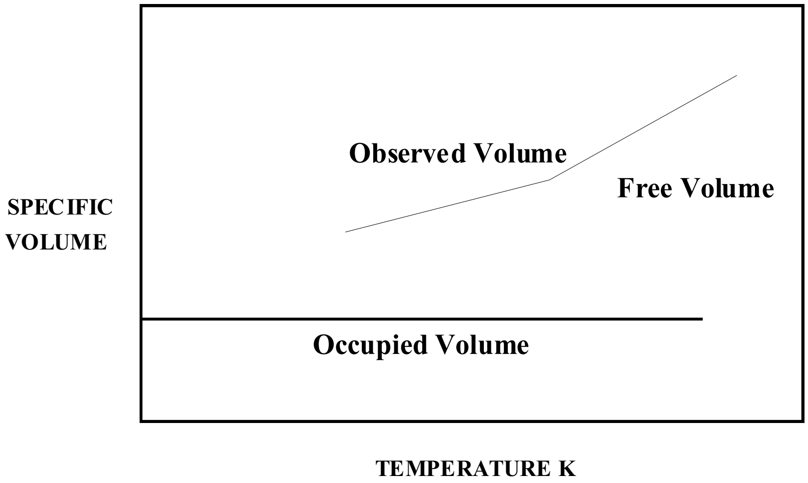


Fig. 4 Free volume theory of plasticization

4. Mechanistic theory

The mechanistic theory of plasticization (also referred to as solvation- desolvation equilibrium) supplements the other three theories previously discussed. This theory can be depicted as having some resemblance to gel theory. The essential difference is that in the gel theory, the plasticizer stays attached to a site along the polymer chain, whereas the mechanistic theory states the plasticizer can move from one polymer location to another.

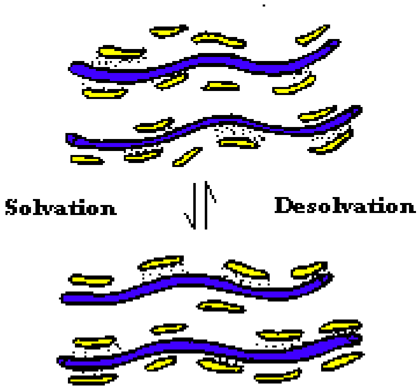


Fig. 5 Mechanistic theory of plasticization

Compatibility

If plasticizer–polymer compatibility is correct, the two materials will form a homogeneous mixture during processing and once cured, the plasticizer will remain in the compound upon cooling and resting at low temperature. From a practical standpoint, it is only necessary that the compatibility be observed at a plasticizer quantity suitable to produce the desired effect. To achieve a high degree of plasticizer compatibility, it is generally necessary that the plasticizer and polymer have approximately the same polarity.

Previously, plasticizers were described as solvents of moderately high molecular weight and low volatility. Their ability to achieve and maintain compatibility with the polymer depends on the same factors that govern the behavior of simpler organic solvents and solutes. The thermodynamic basis for such interactions is expressed by Hildebrand solubility parameters, defined as the square root of cohesive energy density. Plasticizer compatibility with an amorphous polymer (or the amorphous phase of a partially crystalline polymer), δ, normally requires values that do not differ by more than ± 1.5 (cal./cc). Solubility parameters for both polymers and plasticizers are conveniently calculated by the additive method of Small, who derived individual parameters for various atoms and groups in the molecules.[8] Compilations of molar attraction constants, commonly known as Small's constants, are given in many handbooks. Table II lists polymers and plasticizers from high to low polarity.[9]

TABLE II
Polymer/Plasticizer Polarity Chart

HIGH

Polymer

Nylon 6/6
Nylon 6
Cellulose acetate
NBR (50% ACR)
Polyurethane
NBR 40% ACR
Nitrocellulose
Epoxy
Polycarbonate
Acrylic (PMMA)
Polyvinyl acetate
NBR (30% ACN)
Acrylate elastomers
Polyvinyl butyral
Epichlorohydrin
Chlorosulfonated polyethylene
Polyvinyl chloride
Cellulose acetate butyrate
Polystyrene
Polychloroprene
NBR (20% ACN)
Chlorinated polyethylene
Highly saturated nitrile
SBR
Polybutadiene
Natural rubber
Halogenated butyl
EPDM
EPR
Butyl
Fluorinated polymers
Silicone

Plasticizer Class

Aromatic sulfonamides
Aromatic phosphate esters
Alkyl phosphate esters
Dialkylether aromatic esters
Polymeric plasticizers
Dialkylether diesters
Polyglycol diesters
Tricarboxylic esters
Polyester resins
Aromatic diesters
Aromatic triesters (trimellitates)
Aliphatic diesters
Epoxidized esters
Chlorinated hydrocarbons
Aromatic oils
Alkylether monoesters
Naphthenic oils
Alkyl monoesters
Paraffinic oils
Silicone oils

LOW

Plasticizer - polymer interactives

Effect of polymer crystallinity

Plasticization takes place primarily in the amorphous phase of polymers and it is here that plasticizers exert their characteristic effect of lowering the Tg. Many highly crystalline polymers will accept only small amounts of plasticizers having similar values if their crystalline structure remains intact. Conversely, if highly plasticized melts are held at temperatures below the melting point, extensive crystallization will occur and the plasticizer will be forced out of the crystalline polymer.

Selection of ester plasticizer

Ester plasticizers find significant use in nitrile, polychloroprene and chlorosulfonated polyethylene elastomers that are used at temperatures of 135°C maximum. Chlorinated polyethylene, epichlorohydrin, acrylic and hydrogenated nitrile will accept the highly polar plasticizers but with service temperatures ranging up to 177°C will use smaller quantities and allow a more limited plasticizer choice because of plasticizer volatility characteristics. Fluorocarbon elastomers will accept a relatively wide range of ester plasticizers, but here, with both the high temperature post cure and application temperatures ranging to 232°C, they find use only at very low levels for processing.

The selection of an ester plasticizer can often be confusing because of the large choice available. As mentioned earlier, plasticizers are selected based on their processing and end-product property contributions. Plasticizer/elastomer compatibility is the major determining factor relative to processing. End-product properties are the other major factors involved in plasticizer choice. Ester plasticizers are divided into two broad groups:

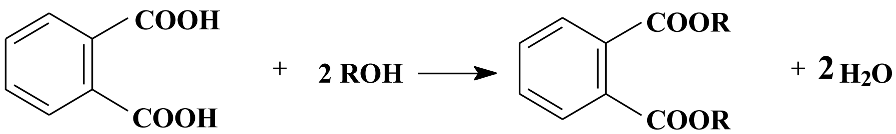
1) Phthalates
2) Specialties

Phthalate plasticizers have approximately 70 percent of the market. Because of their low cost and high volume, they are referred to as commodity plasticizers. Specialty plasticizers may be used alone in compound but, because of their price, are frequently used in combination with phthalate esters. The primary purpose for specialty esters is to have performance properties not achievable with the phthalate esters. There are additional ways of dividing specialty esters:

1) Low Temperature (monomerics)
2) High Temperature
3) Permanent

Phthalates (general purpose ester plasticizers)

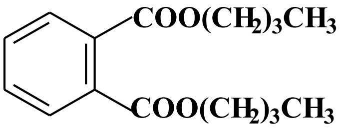
The phthalates are organic esters of phthalic acid and alcohols. In describing ester plasticizers, the structures of the phthalates are more limited than those of the specialty esters. This occurs for two reasons: 1) there was only one acid to deal with, and 2) the major thrust of phthalates was low cost and the alcohols of greatest commercial availability are least expensive. In actual practice, phthalic anhydride is used rather than phthalic acid, as there is a greater return upon charging and less water to expel at the end of the esterification.



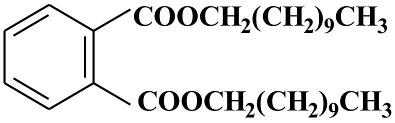
For general purpose plasticizers, the alcohol ranges from butyl (C-4) to the undecyl (C-11) groups. Some products are synthesized with mixed alcohols, varying carbon chain lengths. The following list shows phthalates that either are currently commercially available or have been in recent years.

Phthalate	Abbreviation
Di-n-butyl phthalate	DBP
Diisobutyl phthalate	DIBP
Di-n-hexyl phthalate	DHXP
Di-n-hepytl phthalate	DHP
Di-2-ethylhexyl phthalate	DOP
7C9C-phthalate (linear and branched)	79P
Diisoctyl phthalate	DIOP
Linear 6C,8C,10C phthalate	610P
Diisononyl phthalate	DINP
Linear 8C-10C phthalate	810P
Linear 7C-11C phthalate	711P
Diisodecyl phthalate	DIDP
Diundecyl phthalate	DUP

To select a phthalate ester from the above list, it is necessary to consider chemical structure. It is relatively simple for those materials as there are really only two variables: 1) the number of carbon atoms of the alcohol portion of the molecule and 2) the degree of branching of the side chains. What is given here for those two variables will apply later when we look at specialty esters.



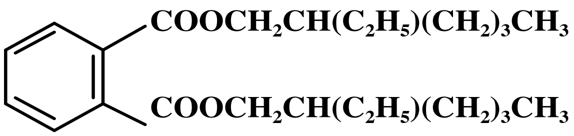
Di-n-butyl phthalate (DBP), C-4



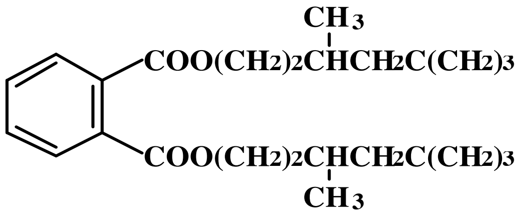
Diundecyl phthalate (DUP), C-11

(Note): The compound properties of phthalates made with mixed alcohols will be very similar to those of the average carbon number. Thus, 79P will perform like a C-8 and 911P like a C-10.

Chain branching – examples are in DOP and DINP:



Di-2-ethyhexyl phthalate, DOP



Diisononyl phthalate (di-3,5,5-trimethylhexyl phthalate) or DINP

Some general statements can be made about the various phthalate esters in relation to their carbon content, referred to as their carbon number, and chain branching. Increasing the carbon number of the alcohol portion of the molecule results in decreasing the plasticizer polarity and gives the following property changes:

- Reduced compatibility
- Poorer processability
- Higher oil solubility
- Higher plasticizer viscosity
- Reduced volatility
- Reduced water solubility
- Better low-temperature flexibility

Increasing the chain branching gives:

- Poorer low-temperature performance
- Increasing volatility
- Lower stability to oxidation
- Higher electrical volume resistivity in compound (poorer conductivity)

Nitrile is the most important elastomer for ester plasticizers as relates to their total consumption. Phthalates head the list for volume of esters used. Phthalates help to provide nitrile a relatively good balance of volatility resistance, moisture resistance and acid/chemical stability.

When used at the amounts of 20 PPHR and 50 PPHR in NBR, phthalate esters in the C-8 to C-10 alcohol range show few differences, except for compound volatility. Table III gives data for compound volatility using those plasticizer contents in a 34 percent ACN polymer.

TABLE III

Compound **Plasticizer**	**1** **DOP**	**2** **6-10P**	**3** **DINP**	**4** **711P**	**5** **DIDP**
Air Oven Aging: 70 h at 125°C					
at 20 PPHR					
Weight Change, %	-9.2	-3.3	-4.2	-4.4	-3.8
at 50 PPHR					
Weight Change, %	-11	-3.6	-4.5	-4.8	-4.1

While phthalate esters may be low cost, they often do not provide the performance needed. Specialty esters are often used in combination with phthalate esters to provide a balance of performance and cost. Depending upon the performance required, specialty esters are often used as the only plasticizer.

Low-temperature esters

Low-temperature plasticizers are used to give improved flexibility and resistance to cracking at low temperatures. Low-temperature plasticizers are generally aliphatic diesters and are typically synthesized with linear dibasic acids. The general structure formula is:

$$\mathbf{ROOC\text{-}(CH_2)_n\text{-}COOR}$$

The most popular dicarboxylic acids are glutaric (C-5), adipic (C-6), azelaic (C-8) and sebacic (C-10). The majority of diesters are manufactured from branched-chain alcohols, such as 2-ethylhexanol or isodecanol. Linear alcohols are normally avoided, as their esters tend to crystallize at relatively high temperatures. Other low-temperature plasticizers are monoesters, such as butyl oleate or 2-ethylhexyl oleate. The monoesters are especially effective in providing low temperature in polychloroprene.

Several other specialty plasticizers offer low temperature to elastomers. Esters based on triethylene glycol, tetraethylene glycol reacted with acids such as capric-caprylic (C-9) and 2 ethylhexanoic (C-8) are excellent for providing low temperature to NBR and CR. Glycol ether esters of adipic acid and sebacic acid provide excellent low-temperature properties to a wide range of elastomers and have low volatility, thus expanding the effective use of the esters over a wide range of temperatures. Following is a list of the low-temperature plasticizers most commonly used in elastomer compounding.

Chemical Name	**Abbreviation**
Diisodecyl glutarate	DIDG
Di-2-ethylhexyl adipate	DOA
Di-2-ethylhexyl azelate	DOZ
Di-2-ethylhexyl sebacate	DOS
Di-n-butyl sebacate	DBS
Diisodecyl adipate	DIDA
Triethylene glycol caprate-caprylate	-
Triethylene glycol 2-ethylhexanote	-
Dibutoxyethyl adipate	DBEA
Dibutoxyethoxyethyl adipate	DBEEA
Dibutoxyethoxyethyl Formal	-
Dibutoxyethoxyethyl sebacate	DBEES

Most of these esters provide nearly equal low-temperature properties, but what distinguishes them is other performance properties such as volatility. In Table IV, examples of six plasticizers are compared for low-temperature performance, before and after heat aging. DOP is used as a standard control in this study.

TABLE IV

Low-temperature brittleness (ASTM D2137), °C for NBR compounds containing Monomeric plasticizers tested after exposures shown.
Compound: 34% [-C≡N] NBR, 20 PPHR plasticizer (10.2% of compound).

Monomerics	**DOP**	**DOA**	**DBEA**	**DBEEA**	**DBES**	**Triethylene Glycol Caprate Caprylates**
As molded	-33	-42	-43	-40	-39	-42
After air oven, 70 h/125°C	-25	-23	-27	-31	-34	-30
Avg. molec. weight	391	373	346	494	505	430

Figure 6 summarizes the compound property trends of low-temperature esters.

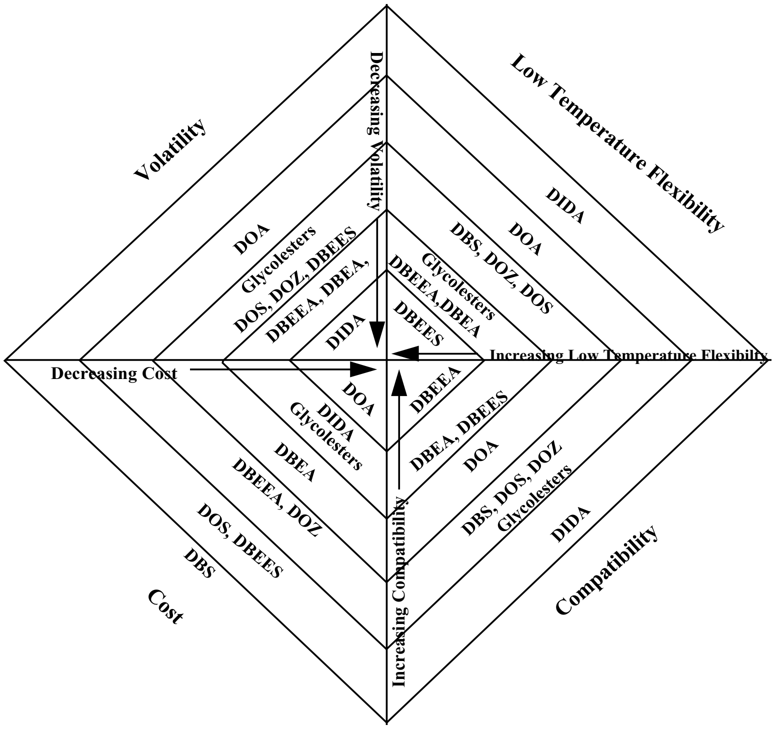


Fig. 6. - Low-temperature ester composite

High-temperature esters

High-temperature esters are used in compounds whose laboratory test temperatures are 177°C, with occasional excursions to 191°C, and where test times are in excess of the normal 70 hours. The environment may be high-temperature air or fluids. These high-temperature esters, monomeric and polymeric polyesters, are less efficient for hardness and processing than general purpose phthalates and low-temperature specialty esters. High-temperature monomerics include trimellitate and pentaerythritol esters.

Trimellitates are commonly used for their excellent volatility resistance during air aging. They also have good resistance to aqueous media. With respect to structure-related properties, they may be synthesized with either linear or branched alcohols. The same trends for alcohol types apply to the trimellitates; linear alcohols provide better low temperature, efficiency and oxidation resistance than branched alcohols.

Chemical Name	Jargon Identification
Tri-2-ethylhexyl trimellitate (tri octyl trimellitate)	TOTM
Tri-(7C-9C(linear)) trimellitate	79TM
Tri-(8C-10C(linear)) trimellitate	8-10TM

Pentaerythritol esters are good plasticizers for severe applications having good resistance to oil extraction and good oxidative stability. They generally are more expensive than trimellitates.

Polymeric polyesters

Polymeric plasticizers offer low volatility, resistance to extraction from elastomer compounds by hydrocarbon fluids and, dependent upon choice of product, resistance to surface marring of ABS and polystyrene plastics. Thus, polymeric polyesters are used in a broad variety of rubber industry applications requiring plasticizer permanence. Some polymerics will allow compound contact with polycarbonate, the result being non stress-cracking. Table V compares monomeric and polymeric ester plasticized compound performance trends.

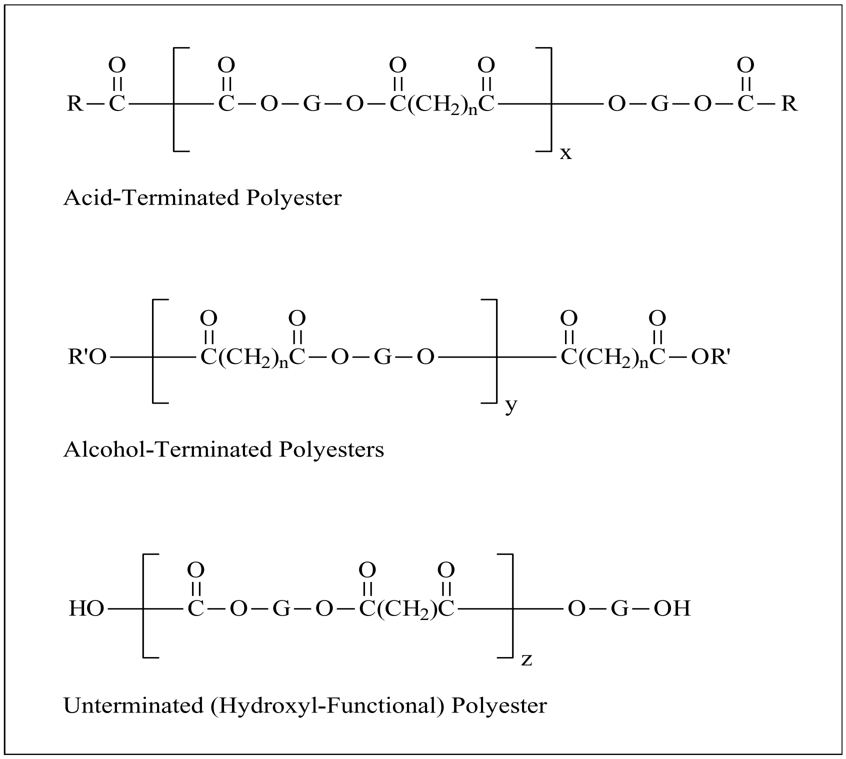
TABLE V

Compound Performance Trends
Monomeric/Polymeric Plasticizers

Property Trend	Monomeric	Polymeric
Processing	Good to Excellent	Fair to Excellent
Compatibility	Dependent upon Chemical Structure	Dependent upon Chemical Structure
Softening Efficiency	Good to Excellent	Fair to Excellent
Low Temperature Flexibility	Good to Excellent	Poor to Fair
Extraction Resistance		
Aqueous	Fair to Excellent	Poor to Good
Organic	Poor	Good to Excellent
Volatility Resistance	Poor to Good	Good to Excellent

Polymeric polyesters are subject to the same trends as monomeric esters as relates to structure, polarity and molecular weight. Generally, viscosity is referenced in place of molecular weight of polymeric plasticizers. The higher the viscosity, the greater the permanence. Polymeric polyesters are composed of regularly alternating dibasic acids and glycols. Glycols are usually 2–5 carbons, and dibasic acids are usually 4–10 carbons. The higher the carbon number, the less polar the polymeric, just as with monomerics. An easier way to compare the polarity of polymerics is to use the saponification value (SV). Using nitrile rubber as an example, the highest SV polymerics are the most compatible with high acrylo NBR (40–50 percent acrylonitrile), and the lowest SV polymerics are compatible with low acrylo NBR (20–24 percent acrylonitrile); the lower the SV, the lower the polarity. Branching results in better permanence during fluid aging as it tends to hinder mobility because of polymer entanglements. While polymerics are generally not used for their low temperature contribution, normal configuration acids and glycols will provide better low temperature than branched chain materials.[10]

As stated above, polyester polymerics are composed of alternating dibasic acids and glycols. This reaction is terminated in one of three ways: 1) introducing monobasic acid, 2) introducing alcohol or 3) overcharging one or the other of the primary reactants. In practice, all three are used. Figure 7 shows these three structures.



$$R-\overset{O}{\overset{\|}{C}}-\left[\overset{O}{\overset{\|}{C}}-O-G-O-\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}\right]_x-O-G-O-\overset{O}{\overset{\|}{C}}-R$$

$$R'O-\left[\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}-O-G-O\right]_y-\overset{O}{\overset{\|}{C}}(CH_2)_n\overset{O}{\overset{\|}{C}}-OR'$$

$$HO-\left[\overset{O}{\overset{\|}{C}}-O-G-O-\overset{O}{\overset{\|}{C}}(CH_2)\overset{O}{\overset{\|}{C}}\right]_z-O-G-OH$$

Fig. 7. - Basic chemical structures of polyester plasticizers

Flame-retardant plasticizers

Flame-retardant plasticizers, phosphate esters and chlorinated paraffins are often combined in usage with flame-retardant plasticizers frequently used in combination with specialty monomeric esters. Both materials are inefficient plasticizers, thus explaining their combinations with specialty monomerics. Chlorinated paraffins are frequently used with antimony oxide to optimize their value as flame retardants. Phosphate esters are frequently used with anhydrous alumina to optimize their flame retarding value. The phosphate ester may contain all aryl, mixed aryl-alkyl or all alkyl groups. Aryl groups are smoke generators; alkyl groups do not produce black smoke. Black smoke may be converted to white smoke by incorporating magnesium hydroxide in the recipe. Chlorinated paraffins generate copious amounts of black smoke when burning. Following is a comprehensive list of phosphate esters commercially available.

Triethyl phosphate

Tributyl phosphate

Trioctyl phosphate

Triisopropyl phenyl phosphate

2-ethylhexyl diphenyl phosphate

Isodecyl diphenyl phosphate

Triphenyl phosphate

Tributoxyethyl phosphate

Butylphenyl diphenyl phosphate

Cresyl diphenyl phosphate

Isopropylphenyl diphenyl phosphate

Tricresyl phosphate

Triaryl phosphate synthetic

Tris(-chloroethyl) phosphate

Chlorinated organic phosphate

Tris(dichloropropyl) phosphate

Trixylenyl phosphate

Diphenyl octyl phosphate

Polymeric ester - high performance applications

Polymeric esters are used in many high-performance elastomer applications that require a combination of low volatility and extraction resistance to various fluids. Rubber applications in underhood automotive applications must retain their effective use over long time periods. Polymeric esters are especially suited for high-performance elastomers such as nitrile, chlorosulfonated polyethylene, high saturated nitrile, polyacrylates, acrylics and nonpost-cured fluoroelastomers.

An example of how polymeric esters can enhance a high-performance elastomer is depicted in Figure 8. High saturated nitrile is used in applications requiring air and fluid resistance. The use of 8-10 trimellitate is well documented as a suitable plasticizer for HNBR. As the graph shows, a phthalate/adipate polymeric ester with a molecular weight of 1000 is very durable for long-term heat aging.

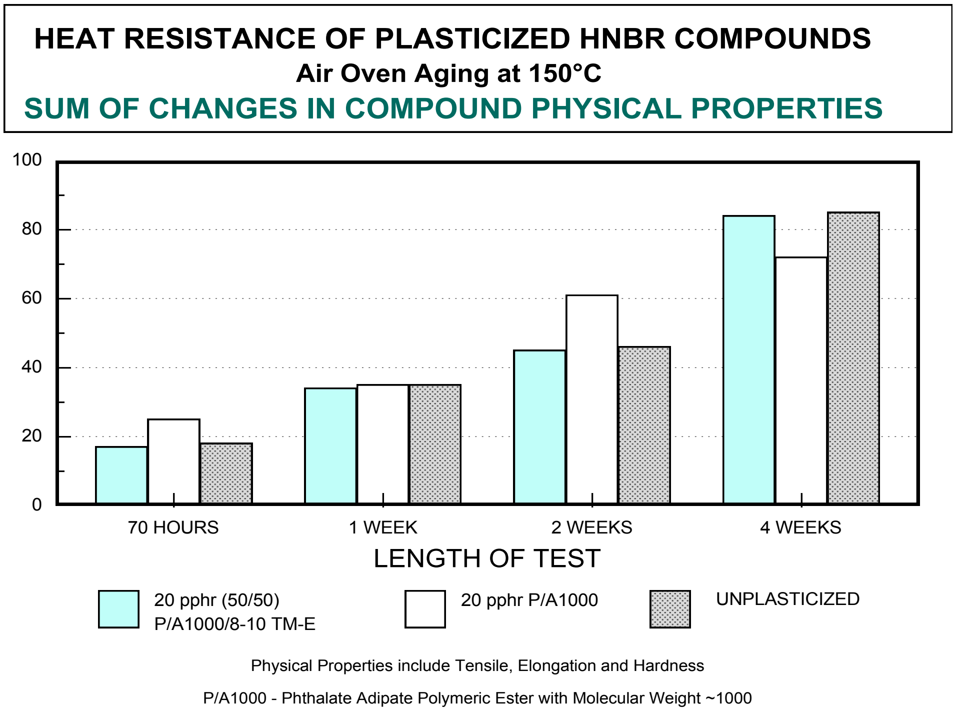


Fig. 8. - Heat resistance of plasticized HNBR compounds

Polymeric polyesters are difficult to categorize by performance due to their varying structure and molecular weight. Table VI classifies the polymeric esters by their general performance trends. Within a given acid type, as molecular weight increases or branching appears, property trends change.

TABLE VI

Comparison of Polymeric Plasticizers

Acid Type	Excellent	Good	Fair	Poor
Glutarates	Compatibility Humidity and Migration resistance Extraction resistance	Non-volatility	Plasticizing efficiency	Low temperature
Adipates	-----	Compatibility Plasticizing efficiency Low temperature Non volatility Extraction resistance	Migration resistance	Humidity resistance
Azelates	Compatibility Plasticizing efficiency Low temperature	Non volatility Migration resistance Extraction	-----	-----
Sebacates	Compatibility Plasticizing efficiency Low temperature Humidity Migration and Extraction resistance	Non volatility	-----	-----
Phthalates	Compatibility Humidity resistance	Non-volatility	Extraction and Migration resistance	Plasticizing efficiency Low temperature

Summary

The basic function of an ester plasticizer is to modify a polymer or resin to enhance its utility. Ester plasticizers make it possible to process elastomers easily while also providing flexibility in the end-use product. Plasticizer–elastomer interactions are governed by many factors, such as solubility parameter, molecular weight and chemical structure. Ester plasticizers are selected based upon a cost/performance evaluation. The rubber compounder must evaluate ester plasticizers for compatibility, processability, permanence and performance properties. The study of these properties by the rubber compounder will help in selecting an ester plasticizer.

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