TECHNOLOGY WATCH: PLASTICIZERS

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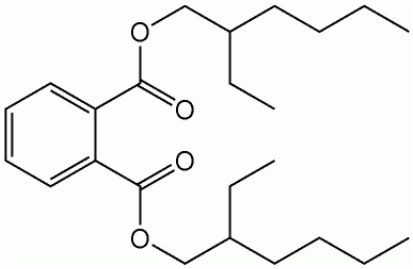
About Plasticizers.

Plasticizers are additives used to improve properties and processing characteristics of polymers. These chemicals can be thought of as high boiling solvents which, when used in relatively large amounts, will increase the molar volume of the polymer thereby reducing melt viscosity and glass transition temperature. Typically, using plasticizers will lower the stiffness and increase the elongation and tear strength of the polymer. They also change melt characteristics thereby allowing for lower temperature processing.

Plasticizers are used in many polymers and for many applications but about 90% of global plasticizer production is used to produce flexible PVC[1]. Using 30% or more of a plasticizer in a PVC composition can turn the polymer from the well-known stiff brittle plastic into a flexible or even soft elastomer useful for shoe soles, children's toys, medical equipment etc. Smaller amounts of plasticizers are also used in other polymers like acrylics, polyolefines, thermoplastic polyurethanes and the like.

Note: the term plasticizer is often used for concrete additives ("super plasticizers") and for the extender oils or 'softeners' used in rubber formulations. These compounds are not the subject of this technology watch.



DEHP, a typical phthalate plasticizer

The most common type of plasticizers available are the phthalates: diesters of phthalic acid. Examples of commercially important phthalate plasticizers include diisononyl phthalate, di-2-ethylhexyl-phthalate and dioctyl phthalate. Many more types of phthalates have been developed over time, differing in molecular weight and type of side chains. The table shows a small number of commonly used phthalate and their abbreviations.

In recent years it was discovered that some of the low molecular weight phthalates can act as endocrine disruptors[2] – meaning they can interfere with human hormone systems. These phthalates have therefore been banned from a number of critical applications like medical, food and toy applications where they can pose health risks.

Apart from phthalates many more types of plasticizers have been known and used for a long time: aliphatic diesters like adipic, azaleic diesters, phosphates like tricresyl phophates which can improve flammability and low molecular weight polymers, usually polyester oligomers. None of these classes are as commercially significant as the phthalates.

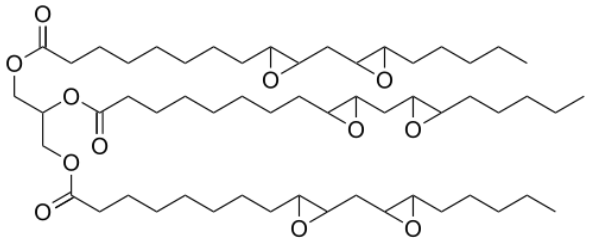
Low Molecular weight	
DEHP	Di(2-ethylhexyl)Phthalate
DBP	Dibutyl Phthalate
DIBP	Diisobutyl Phthalate
BBP	n-butyl benzyl phthalate
High Molecular Weight	
DINP	Diisononyl Phthalate
DIDP	Diisodecyl Phthalate
DPHP	Dipropylheptyl Phthalate

Some common phthalate plasticizers

Trends in plasticizer research and development

When looking at the recently published patent literature, two main trends can immediately be noticed. The first is that practically all new applications are about non-phthalate systems and the second main trend is that about 50% or more- of the industrial research on plasticizers is towards renewable resources.

The use of **natural-oil** based chemicals is arguably one of the most important trends in the polymer industry. The use of natural oils as an energy source has repercussions for the chemical industry making a number of bio-based chemicals more readily available. Biodiesel is produced by transesterification of natural oils (lipids) with monoalcohols like methanol or poropanol resulting in fatty acid esters and glycerol. All sorts of natural oils can be used but most commonly used oils are soybean oil, linseed oil, sunflower oil, castor oil, corn oil, canola oil, rapeseed oil, palm kernel oil, cottonseed oil, peanut oil, coconut oil, palm oil, tung oil, safflower oil. The use of natural oil derivatives in plasticizers is a big trend in the industry.



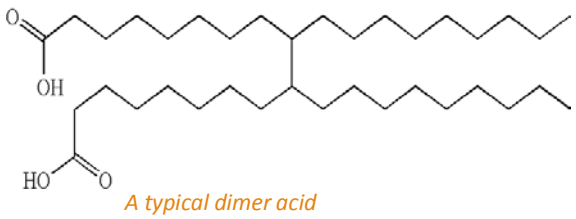
Epoxidized Linseed Oil

Unmodified oils or fatty acids cannot be used as plasticizers for polar polymers like PVC because they not compatible. By modifying through e.g. epoxidization, the oils or fatty acids can be made more polar and more compatible. Epoxidized **vegetable oils** and epoxidized **fatty acids** may be obtained by oxidizing vegetable oils and fatty acids with peroxide acids.

Dow Chemicals is especially active in the field of "vegetable oil"plasticizers[3,4] using especially soybean oil derived acids of which there is a huge production in the US. Also some universities are active in this field like the University of Minnesota[5] and the University of Malaya (palm oil).

Apart from epoxidizing, other methods have been patented to make natural oils or the derived fatty acid esters more compatible with polar polymers such as PVC. An example is acetylation. Acetylated castor oil or acetylated stearate esters have been file as plasticizers[6] (Dow). Reacting oils with polyols and acid anhydrides to make "alkyds" useful as plasticizers has also been filed e.g. for palm oil[7] (Univ. of Malaya).

Dimerized fatty acids are well known in the oleochemical industry and may be obtained from monomeric unsaturated fatty acids by an oligomerisation reaction. These materials have also been modified, e.g. by DSM for use as PET plasticizers[8].



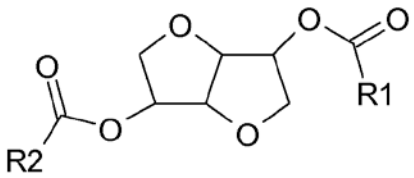
A typical dimer acid

Not surprisingly, **glycerol**, which is a by-product of biodiesel production is used as well to produce novel plasticizers. Especially ExxonMobile[9,10] appears to be active in the field of glycerol-based plasticizers. Plasticizers can be made from glycerol by esterification with acids, making triglycerids. Unlike the natural triglycerids which make up natural oils, a wider choice of side chains is available for synthetic triglycerids. Compatibility and other plasticizer properties can be tuned by choosing the correct side chains: longer, shorter branched or functional.

Glycerol esterified with short chain acids, like e.g. glyceroltriactetate ("triacetin") can also be used as plasticizers for certain polymer like e.g. for thermoplastic polyurethanes as shown by BASF[11].

Also related are 1,3-dihydroxyacetone esters as filed by Boston Polymer[12].

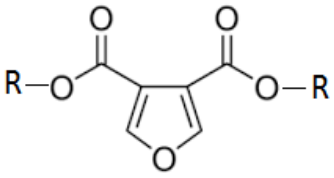
Carbohydrates are another class of bio-renewable compounds that are used in novel plasticizer development. Examples are the dianhydrohexitol diesters of 2-ethylheptanoic acid which are claimed by Evonik to be useful as PVC plasticizers[13].



Dianhydrohexitol (sorbitol) diester

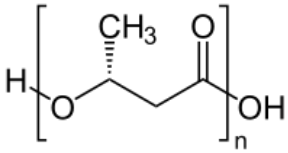
BASF[14], Dow[15], Evonik[16] and others have filed patent applications on the use of **furan** derivatives as plasticizers, especially 2,5-dicarboxylates of furan and tetrahydrofuran are said to be effective as plasticizers for PVC and other polymers. Furan and derivatives can be produced both from renewable as from petroleum-based feedstock.

Terpenes which are a class of chemicals found in plant resins can – according to some patent applications- also be used as plasticizers. Derivatives of myrcene and faresene can be modified through Diels-Alder reactions with e.g. maleic anhydride as dienophile to make them more compatible with polar polymers[17].



Furandicarboxylate

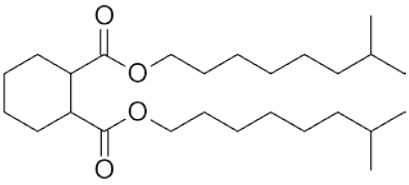
DuPont is the biggest producer of bio-based 1,3-**propanediol** and has a patent application on the use of polytrimethyleneetherglycolesters derived from this for use as platicizers with a "variety of base polymers"[18]. Other bio-based low molecular weight polymers that have been patented as plasticizers are **polyhydroxyalkanoates**[19], **lactide** oligomers[20], and lacton-based hyperbranched polymers[21].



Poly(trimethylenether)glycol

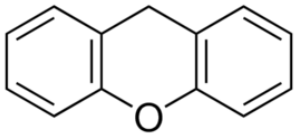
Of course there is still research going on on conventional petroleum-based non-phthalate compounds, especially by larger cooperations. **Benzoates** appear to be a speciality of Emerald. For example 1,2-propyleneglycol dibenzoate blended with other chemicals like DEG and DPG is said to be useful for a number of polymers both thermoplastic and thermoset[22,23].

Cathechol diesters[24] will of also act as plasticizers as patented by ExxonMobil. The same goes for **cyclohexanedicarboxylates,** which are in effect the saturated form of phthalates and are believed to be non-toxic and suitable for food-related applications. Examples are diisononyl 1,2-cyclohexanedicarboxylate (DINCH) esters by Evonik[25] and by BASF[26].



Diisononyl 1,2-cyclohexanedicarboxylate (DINCH)

Among the non-biobased polymeric plasticizers **polyphthalates** have been filed as plasticizers for PVC and are said to be stable and show no environmental or health problems[27]. Other interesting compounds claimed to be useful as plasticizers are based on **xanthenes**[28] .



Xanthene

Conlusion

The environmental problems with the low molecular weight phthalate plasticizers have prompted the industry to innovate. A host of new plasticizers have been invented during the recent years, the most notable trend being that a lot of them are based on renewable resources.

[1] http://www.plasticisers.org/en_GB/media-publications/publications/factsheets/plasticisers-flexible-pvc
[2] http://www.plasticisers.org/en_GB/health
[3] WO2014/149723
[4] WO2011/041396
[5] WO2012/036913
[6] WO2013/191812
[7] WO2015/047077
[8] WO2012/080163
[9] WO2010/110911
[10] WO2010/074737
[11] WO2011/141408
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[18] WO2015/023714
[19] WO2013/156930
[20] WO2012/131252
[21] WO2012/121553
[22] WO2014/143902
[23] US20130274396
[24] WO2015/065691
[25] US20130310471
[26] WO2010/063740
[27] WO2013/116818
[28] WO2010/070588

For an extensive list of recent plasticizer-related patent applications contact gbleys@PURpatents.com