INERIS
controlling risks for sustainable development

National helpdesk
Chemicals substitution

Newsletter

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Special feature

Polybenzoxazine and polybismaleimide resins: «high-performance» resins synthesized from bisphenols

The synthesis of materials intended for «high-performance» applications may involve bisphenols, which are benzoxazine resins and polybismaleimide resins.

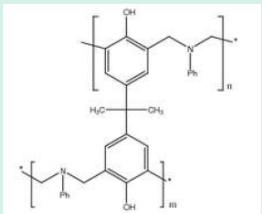
Benzoxazine resins, or polybenzoxazines, are derived from the polymerization of benzoxazine monomers, which are synthesized essentially from formaldehyde, a substance having a phenol group (such as bisphenol A or bisphenol F), and a substance having a functional amine group (e.g., aniline).

Due to their properties (low viscosity when hot, high glass transition temperature, good thermal stability, good mechanical strength, low water absorption, low dielectric constant, fire behavior), benzoxazine resins find «high-performance» applications in various sectors, such as electronics (printed circuit boards), aerospace, and transportation (primary, secondary structures[1], and interior aircraft panels, parts located near the engine).

The use of those resins is rapidly developing, but it appears that they have not yet reached the level of technological maturity required for industrial deployment. We can expect substantial future development, especially in aeronautical applications.

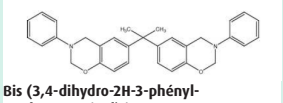
There are different bisphenol-based benzoxazine resins on the market:

- benzoxazine [BA-a] resins based on bisphenol A ;
- benzoxazine [BF-a] resins based on de bisphenol F ;
- benzoxazine [Boz-BP] and benzoxazine [B-adi] resins based on N phenyl phénolphtalein (also of the bisphenol family).



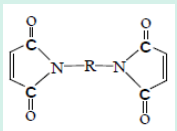
Benzoxazine BA-a resin pattern

The most common benzoxazine resins are the [BA-a] resins, which are obtained through polymerization of a monomer synthesized from BPA: bis (3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl) isopropane



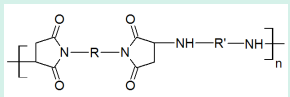
Bis (3,4-dihydro-2H-3-phényl-1,3-benzoxazinyl) isopropane

Polybismaleimide thermosetting resins (or BMI resins), from the polyimide family, can be obtained through polymerization of bismaleimides and reactive comonomers: aromatic amines, vinyl and allyl compounds, isocyanates[2] and allylphenols; it can be a derivative of BPA, namely diallyl bisphenol-A (CAS number 1745-89-7), in which case they are called BPA-BMI resins.



Bismaleimide pattern

Like benzoxazine resins, polybismaleimide resins can be used for "high-performance" applications in the electronics (printed circuit boards), transportation, and aerospace sectors (components near the engine, structures).



Structure des résines polybismaléimide

They can be used as matrices for the production of composite materials (with glass or carbon fibers) having good thermal stability, good mechanical strength even at high temperatures (their glass transition temperature can reach 280 °C), excellent electrical properties, and a relatively low tendency to absorb moisture.

The benzoxazine and polybismaleimide resins came into use relatively recently, and there appears to be little activity directed towards the development of production processes without the use of bisphenol-type molecules. However, research is in progress with respect to the benzoxazines to use phloretic acid instead of bisphenol derivatives.

Sources

http://healthcare.evonik.com/product/health-care/en/custom-solutions/custom-manufacturing/bismaleimides/

http://www.hexcel.com/Resources/DataSheets/Prepreg

https://www.compositesworld.com/articles/bmi-and-benzoxazine-battle-for-future-ooa-aerocomposites

https://link.springer.com/chapter/10.1007/978-981-4451-76-5_1

Trejo-Machin A. et al., "Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine " Green Chemistry, vol. 19, no. 21, pp. 5065-5073, 2017

[1] *The primary structure of an airplane is the «vital» structure, i.e., the framework without which the airplane cannot fly (frame, spars, stringers, ribs, engine mounts, coatings, brackets, ...). The secondary structure of an aircraft is the structure that is necessary but not indispensable for flight (supports, fittings, and equipment).*

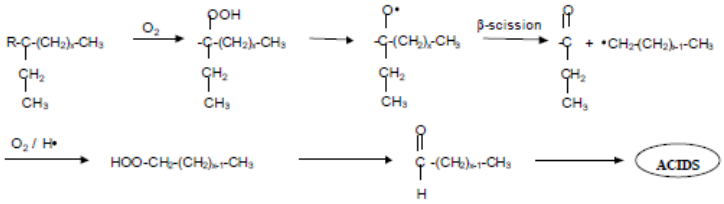
[2] *Diisocyanates may enter into the composition of this monomer; the possible risk of these substances for workers is discussed in the context of the European REACH Regulation*

An alternative to BPA used as an antioxidant for PVC and its plasticizers

During its manufacture, processing, or use, flexible PVC can be exposed to high temperatures, and the same applies to plasticizers that are incorporated into the material (phthalates, terephthalates, DINCH, etc.).

Nevertheless, in the presence of oxygen, the tertiary carbon atoms[3] of the branched plasticizers can undergo auto-oxidation, thus forming low molecular weight acids having no plasticizing properties. Once PVC has been sufficiently stripped of plasticizer, it loses its flexibility and becomes sensitive and vulnerable to mechanical stresses and thus prone to cracking and even breaking.

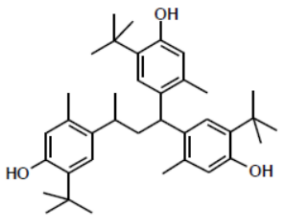
That is why the plasticizers need to be stabilized with an antioxidant. This antioxidant can be incorporated into the PVC during its formulation or it can be integrated into the plasticizer, with its content in the PVC being on the order of 0.3%.



Auto-oxidation reactional mechanism of branched phthalates

The antioxidant, in combination with conventional thermal stabilizers (e.g., salts containing tin or a calcium/zinc mixture), also helps to protect PVC to some extent against dehydrochlorination. At the same time, this strengthens its antioxidant power on plasticizers, since the hydrogen chloride released during the dehydrochlorination of PVC can further accelerate the decomposition thereof. It also acts as a polymerization inhibitor in order to prevent the post-polymerization of the material while it is being treated.

Nowadays, bisphenol A is the antioxidant that is the most used to stabilize branched plasticizers. It should be noted that sterically hindered phenolic antioxidants are also used to a lesser extent. However, the company Addivant proposes LOWINOX CA22, a sterically hindered phenolic antioxidant having the empirical formula 1,1,3-tris (2'-methyl-4'-hydroxy-5'-tbutylphenyl) butane (CAS No 1843-03-4), which could provide an alternative to BPA for these applications.



LOWINOX CA22 (n°CAS : 1843-03-4)

According to Addivant, LOWINOX CA22 has a greater antioxidant potency than BPA and the traditional sterically hindered phenolic antioxidants: it has been tested on various plasticizers with convincing results, including TOTM (Tri Octyl Trimellitate, No CAS : 3319-31-1), having an Oxidation Induction Time (O.I.T.)[4] two to six times higher with LOWINOX CA22 despite using lower concentration levels.

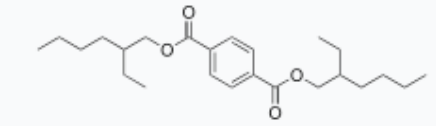
Furthermore, according to tests carried out by Addivant, LOWINOX CA22 would limit the yellowing and discoloration of PVC to a greater extent than traditional sterically hindered BPA and phenolic antioxidants.

Sources

https://polymer-additives.specialchem.com/_/media/product-technical-datasheets/polymer-additives/additive/5173-lowinox-ca22.pdf

A new DOTP production site in Europe

DiOctyl TerePhtalate (DOTP, also referred to as DEHTP) is a plasticizer for PVC able to replace some phthalates (DEHP, DBP, BBP and DIBP) for a wide range of applications, such as electrical connectors, *toys*, fabric coatings, and floor coverings.



DiOctyl TerePhtalate (DOTP, n°CAS: 6422-86-2)

The OXEA Group, a producer of oxo intermediates and oxo derivatives[5], has entered into cooperation with a German partner in order to produce DOTP in Germany. According to the OXEA Group, this unit will have from 2019 an annual production capacity of 60,000 tons of DOTP.

Sources

http://www.oxea-chemicals.com/fileadmin/Page/Unternehmen/Medien/Unternehmens-News/2017/171201_EN_OXEA_steps_up_DOTP_offering_in_Europe.pdf

A new alternative to PVC for respiratory masks

Teknor Apex sells the Medalist® range of thermoplastic elastomers (TPE) capable of replacing flexible PVC for many medical applications (infusion tubes, catheters, infusion bags, films, cables and connectors for medical equipment, etc.).

According to their manufacturer, these TPEs have excellent flexibility and elastic recovery, high strength in the molten state, good tearing resistance, and a wide array of options for sterilization (electron beam, gamma, oxide ethylene, and autoclave).

These elastomers are free of phthalates and BPA and are produced from food-grade, FDA compliant reagents. In addition, these materials meet the criteria of ISO standard 10993-5 for biocompatibility.

Teknor Apex has recently added a new product line to its Medalist® line that is capable of replacing soft PVC: the Medalist® 50100 Series TPEs. This new series makes it possible to add breathing masks and inhalers to already existing applications.

According to Teknor Apex, Medalist® 50100 Series TPEs are more resistant to deformation than PVC and have the same level of transparency as the latter, which makes the monitoring of patients easier.

Sources

https://www.teknorapex.com/medalist-medical-tpes-for-face-masks---product-selector-guide
https://www.teknorapex.com/medalist-tpes-for-medical-devices-products-and-uses

[3] *Carbon atoms bound to three other carbon atoms*
[4] *Time between contact with oxygen and oxidation onset*
[5] *Alcohols, polyols, carboxylic acids, specialty esters, and amines used in the production of coatings, lubricants, cosmetics, and pharmaceuticals, flavors and fragrances, printing inks and plastics*

Coming soon

MEDICA/COMPAMED 2018 in Düsseldorf (Germany) from november 12th to 15th 2018

During the COMPAMED trade fair, international manufacturers will present their latest trends and innovations in tubes, catheters, valves, ...

https://www.medica-tradefair.com/

ALL4PACK exhibition in Paris (France) from november 26th to 29th 2018

The "ALL4PACK Paris" salon brings together actors from the food industries, cosmetics, beauty, health, pharmaceuticals, retail and consumer goods.

https://www.all4pack.com/

POLYMERS IN FLOORING in Berlin (Germany) from december 4th to 5th 2018

Innovations in the field of polymer flooring will be presented for residential, commercial, industrial, sanitary, sports and leisure applications ...

https://www.ami.international/Events/Resources/Programme/Polymers_in_Flooring_EU18.pdf