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Evolving to match the market

Some factors driving changes in the market for epoxy coatings are considered. REACH and other regulations may lead to some widely used raw materials being withdrawn. "Green" concerns are already being addressed in many ways, including improved performance efficiency, wider use of bio-renewable resources and development of low or zero VOC coatings with high performance.

Legislation and environmental issues drive changes in coatings technology
Stephen Jewitt
The term epoxy coatings describes a broad range of products and chemistries based on a common structure (Figure 1) that are used in industrial and protective coatings as well as the construction industry. They can yield products as diverse as electrodeposition primers, can coatings, floor coatings, marine coatings and chemically resistant tank and pipe linings.
For many decades, the driver for development has been to provide the same or better performance at reduced cost. This can be achieved by reducing the product cost itself or reducing the process time, producing the finished item more quickly.
A good illustration would be the application of waterborne epoxy coatings directly onto "green" concrete. The cost of the products may be marginally higher than for a more conventional solvent-free system. However, the traditional 28 days' waiting time prior to coating can be dramatically reduced.
Regulation has also been a driver for change. VOC regulations in Europe over the past 20 years have moved the industry away from higher molecular weight epoxy coatings in solvents towards low VOC coatings based on liquid bisphenol A/bisphenol F epoxy resins. This in turn has created a requirement for low viscosity amine curing agents that are compatible with liquid epoxies.
VOC restrictions have also advanced the use of waterborne epoxy coatings based on solid and liquid epoxy resins dispersed in water. If VOC restrictions are further tightened to 100 g/l or even to zero, the use of waterborne epoxy coatings will further increase.
Alongside these changes in the liquid epoxy coating market, powder coatings, based on high molecular weight solid epoxy resins (n>1) and inherently solvent-free, have shown very high growth over the same period.

True costs of REACH are only starting to be felt
Any analysis of trends and innovations in this market cannot ignore the far-reaching effects of REACH, a regulation that is already in force and that will be rolled out in Europe from now until 2018. It is reasonable to assume that no-one yet knows what effect REACH will have on the EU coating market.
The pre-registration of substances is now completed. Now the task of forming SIEFs (Substance Information Exchange Forums) and performing registrations is well underway. One could alternatively say, it is now that the industry is starting to pay the price of REACH.
The sheer scale of the task is gargantuan. According to the European Chemicals Agency ECHA, as of December 19th 2008, there were "about 150,000 substances pre-registered in REACH by 65,000 companies." Assuming some errors and duplications, a slightly smaller number of SIEFs will share information and costs on these registrations. One of the great uncertainties is how many useful coatings substances will fail to survive past the 2010, 2013 and 2018 registration deadlines.
Clearly some of the most toxic substances (known as CMRs) will be withdrawn altogether. The costs and complexity of the authorisation process for substances of very high concern (SVHCs) will make their continued use uneconomic.
Examples in the epoxy coatings sector are MDA (methylene dianiline, 4,4"-diaminodiphenylmethane, CAS 101-77-9) and dibutyl phthalate (CAS 84-74-2) both of which will probably not survive past the REACH deadline of December 2010. There is also a risk that some of the less toxic but also less profitable or low volume products will be withdrawn later in the REACH process because no-one in the supply chain can afford the costs or the time needed to generate the data required for registration.

Global recession may increase problems of REACH
REACH has come at a critical time when the entire world has fallen on recessionary times. One can argue that the coatings industry, and particularly the automotive and construction industry, has been harder hit than most during the latter part of 2008 and 2009.
Just as some chemical producers will not survive this economic downturn, some coatings chemicals may not survive REACH. Further downstream, the task of reformulation comes at a time when coatings formulators can least afford it.

Green coatings come in many shades
The terms "Green" and "Bio-renewable" have become buzzwords in the coatings industry. But "Green" can mean different things to different people. It can mean "low environmental impact". In this respect, "low emission", "low VOC" and "low CO2 footprint" can all be a part of the greener product image.
The term "Bio-renewable" incorporates the concept of using renewable resources or plant-based chemicals rather than those derived from petroleum. Bio-renewable does not necessarily imply lower toxicity.
Other interpretations of "Green" could be lengthening the lifetime of a coated article or extending the maintenance interval on a steel bridge, for example. "Green" could imply achieving the same performance from a coating with lower film thickness (reducing material usage and carbon emissions).
"Green" could also refer to novel ways of improving the energy efficiency of a building (thermally insulating

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coatings, solar heating (IR absorption) or solar reflective). It could also involve reduced energy requirements in low temperature curing powder coatings. "Green" could even encompass health-related issues such as sick building syndrome or anti-microbial coatings.

Defining "low emission" coatings may not be simple

During the 1990s, a very fashionable media issue was the so-called sick building syndrome, a term used to describe situations in which building occupants experience acute health and comfort effects that appeared to be directly linked to time spent in such a building, though no specific illness or cause could be identified.

One of the main causes was said by the US EPA to be "chemical contaminants from indoor sources". For example, "adhesives, carpeting, upholstery, manufactured wood products, copy machines, pesticides, and cleaning agents that may emit volatile organic compounds (VOCs), including formaldehyde". It also suggested that "Low to moderate levels of multiple VOCs are also thought to produce acute reactions in certain people".

For many decades the construction industry standard for floor coating has been "solvent-free" epoxy. In the main part these floor coatings have been formulated using liquid epoxy resins as well as a variety of reactive and non-reactive diluents and with curing agents that include a variety of substituted phenols as well as benzyl alcohol.

Although benzyl alcohol has a high boiling point (203 °C) and a very low vapour pressure at ambient temperatures, the various global methods of determining VOC predominantly use methods that require heating in an oven. The differences in weight loss between high and low temperature VOC determinations sparked a long-running debate on whether such materials should be exempted in determinations of floor coating VOCs.

There have been many well reasoned arguments over the years, (e.g. the Thermoset Resin Formulators Association (TRFA) in the USA and Deutsche Bauchemie [1] argued that benzyl alcohol should be exempted from such VOC calculations).

New tests assess exposure risks more accurately

The AGBB (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten - Committee for health-related evaluation of building products) and the ISO standard EN ISO 16000 have recently clarified the way that low volatility components should be considered in internal construction areas. VOC (Volatile Organic Compound) and SVOC (Semi-Volatile Organic Compound) emissions are measured over some time using automated analytical techniques.

Substances of concern have been assigned LCI (Lowest Concentration of Interest) values. For example, benzyl alcohol has been assigned an LCI of 440 µg/m3 (for comparison, xylene has an LCI of 2200 µg/m3, butanol 3100 µg/m3 and phenol 78 µg/m3) Emissions from various sources can thus be measured and compared to the volume of the building and the available ventilation.

Future epoxy floor coatings will not only be required to be "solvent-free" but also VOC-free and SVOC free. Products are already on the market that comply with these low emission requirements, i.e. no benzyl alcohol, no phenol or derivatives, no solvents and the use of reactive (fast) amines with low evaporation potential.

However, industry awareness of these requirements remains low and there is no absolute compulsion yet for an architect or building designer to use these low emission products. Notably, they show no reduction in performance. Pull-off tests on a low emission epoxy product applied over wet concrete showed only failure in the concrete substrate (see Figure 2).

Further restrictions on nonyl phenols are likely

Nonyl phenols and other phenols have traditionally been used in epoxy curing agents as an accelerator, particularly useful when products will be applied at temperatures of 15 ºC and below. Although not specifically excluded by REACH, the standards for building products emissions (CEN TC 351/WG 2) and other European initiatives will restrict or even prohibit the use of nonyl phenol and other phenols in floor coatings and protective coatings for interior uses.

The epoxy and curing agent producers have largely solved this issue by developing products that are completely free of phenols (including 4-tert-butylphenol). However, the prices of such products are necessarily a little higher and as a result, uptake by the coatings industry had been relatively slow. Undoubtedly, nonyl phenol use in epoxy coatings will soon be curtailed in Europe.

Bio-based epoxy materials are already in use

Today many epoxy coating raw materials are derived from petrochemicals. However, many useful components can be derived from renewable resources. A good example is production of epichlorhydrin, one of the main precursors for epoxy resins, from glycerine (Figure 3).

Glycerine-based amines can also be used as curing agents in epoxy and polyurea coatings, while glycerine carbonate can be used as a diluent in some epoxy systems. Useful epoxy functional materials can also be derived from sugars such as sorbitol.

Polyamidoamine curing agents have always been produced using dimer acids derived mainly from tall oil, which comes principally from the wood pulping industry. New lower viscosity polyamidoamines with improved performance have recently been introduced and are especially useful in VOC-compliant anti-corrosion coatings. Phenalkamine curing agents, used in low temperature curing epoxy applications, are derived from an extract of cashew nut shell liquid (CNSL).

It could therefore be said that the industry has already made significant progress in the use of renewable materials. This trend will continue, but only if the economics also make sense. Crude oil at USD 50-75 per barrel will not necessarily encourage the use of bio-based materials in the short term. At USD 100+ per barrel, the economics of these bio-based products makes better sense.

Increases in the use of biofuels have increased the availability of glycerine as a by-product. However, using available agricultural land to produce biofuels must be balanced with food production. Further sources of organic materials will therefore be the non-food waste products from agricultural production.

A good example is the production of lignin-based compounds (Figure 4) from straw or corn stalks. Lignins derived from paper pulp production will also become a source of raw materials for the coatings industry. The key

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to unlocking these lignin-based chemicals at low cost is enzymatic processing, which operates at low temperatures.

Waterborne epoxy systems offer high performance

There is no doubt that waterborne epoxy coating systems have increased their market share over recent years and will continue to do so. New products have been introduced that allow direct application to damp concrete and that show controlled water vapour permeability. The latest developments have very low or even zero VOC.

Waterborne systems do, however, offer a greater degree of difficulty for both formulator and applicator alike. Formulated waterborne coatings are also less tolerant to changes in applications conditions (temperature and humidity). Careful formulation and painstaking testing is the key to success.

The suppliers of waterborne epoxies should be congratulated for developing the technology to a stage where it is now widely used in preference to more traditional coatings for certain applications. In concrete coating, the use of waterborne epoxy systems will continue to grow above GDP rates for some years to come. Waterborne systems are now also available that comply with food contact regulations.

Nanotechnology shows some gains and great potential

Nano has been the technological buzz-word of the "noughties" (2000-2009). One would be hard pressed to find an innovator in the coatings industry who has not investigated nanotechnology as a means to improve product performance. Many well established products in the industry already use nanotechnology, sometimes even without the formulator being aware of it.

Almost every major player in the coatings field can now boast an anti-microbial product in their range. Often these are based on waterborne epoxy resins including a silver containing substance (nano silver) and usually according to one of a handful of patent applications.

Other nanoparticles will be utilised by the epoxy coatings industry in the coming years. Nanofibres will be (indeed, are being) used to toughen coatings and give extra fatigue resistance and better edge coverage. Nanomaterials will be used to enhance the response to fire of coatings. Use of nano zinc epoxy may well revolutionise the anti-corrosion industry. However as a footnote, it is essential to be aware of the toxicity implications of using nanoparticles, both in coatings production and in future recycling.

Patterns of change summarised

Prices of many coatings chemicals are likely to rise in Europe due to REACH. Epoxy resins and curing agents will not be immune from this. The availability of some components (especially curing agents) might also be restricted in Europe.

Innovation will continue to be driven by cost reduction. An increase in bio-sourced raw materials will undoubtedly occur. Health and environmental issues will conflict with demands for low cost, particularly in floor coatings. The use of waterborne epoxy coatings will continue to increase in selected applications. í

REFERENCE

[1] Prüfverfahren zur Bestimmung des Masseverlustes und Einordnung eines Epoxidharzsystems als "Total solid" 2008.

Results at a glance

Epoxy coatings form a class of high-performance systems with a very wide range of applications. Some factors driving changes in the market for these products are considered. Stricter regulations on VOC content have led to a greater use of low viscosity/high solids systems, and to improvements in the performance of waterborne epoxies. REACH procedures and other impending legislation will lead to some common raw materials being withdrawn. Several epoxy materials are already based on bio-renewable resources. More products may in future be derived from lignin. Concern over the contribution of volatile coatings ingredients to "sick building syndrome" has led to the introduction of low-temperature long term emission tests and low-emission epoxy floor coatings. Nanotechnology is already in use in coatings systems, and further applications will emerge in the coming years.

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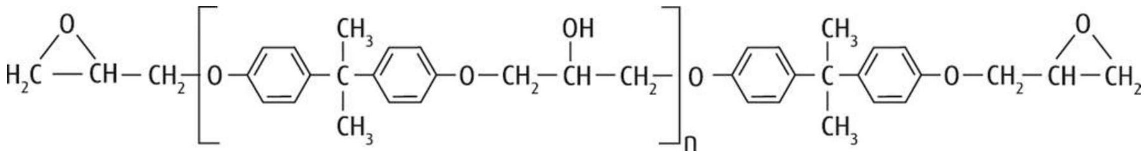

Figure 1: General structure of epoxy resins showing terminal epoxy groups

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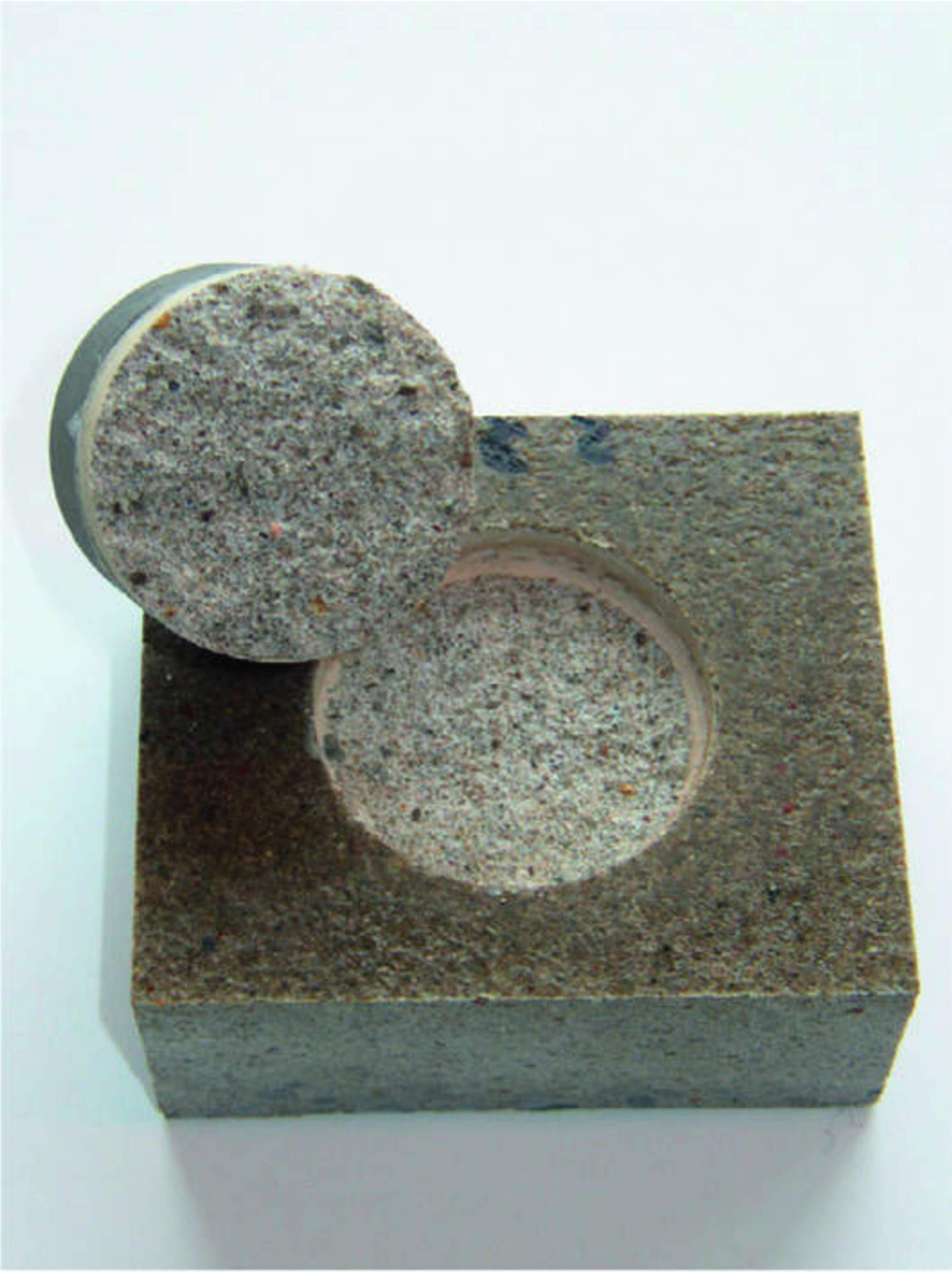

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Figure 2: A low-emission epoxy flooring product shows excellent adhesion to wet concrete

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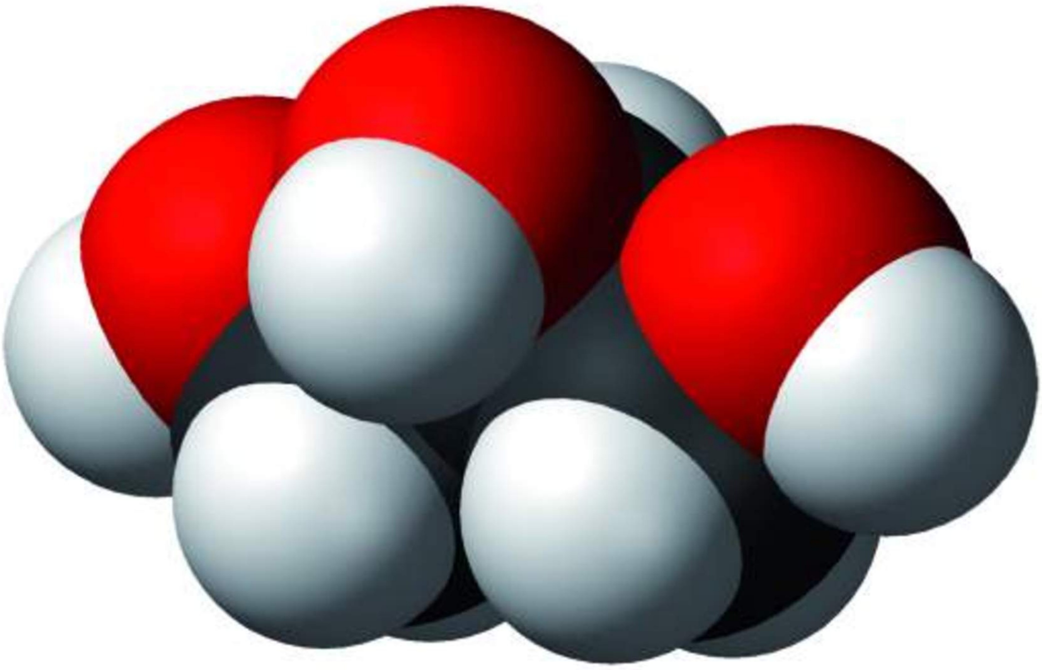

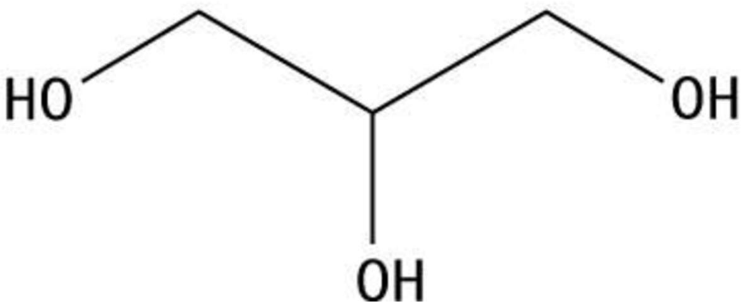

Figure 3: General structure of glycerine

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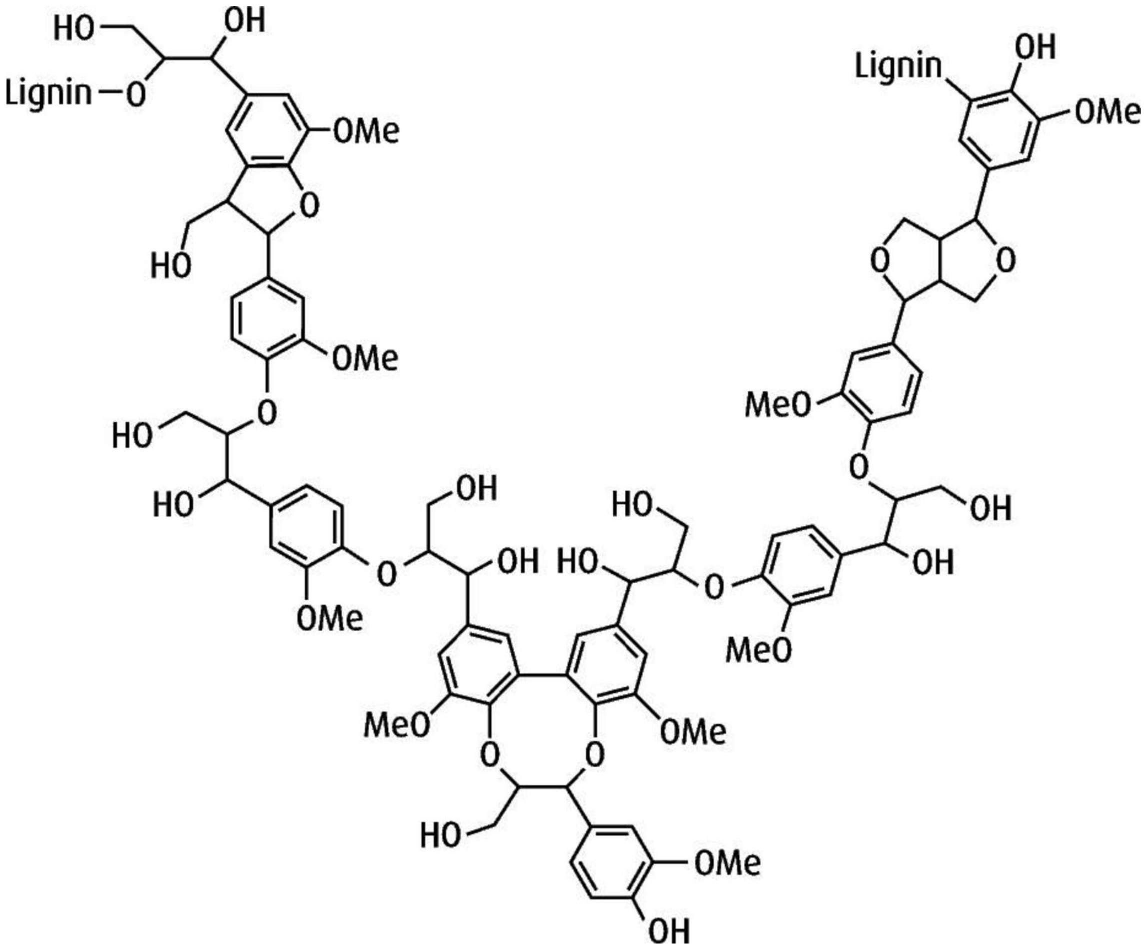

Figure 4: General structure of lignin

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Figure 5: please provide caption