Block Copolymers Enable the Use of Epoxy Resins in Fuel Cells

Empower Epoxy Resins for Hydrogen Applications

Hydrogen tanks and fuel cells are two crucial components for hydrogen-powered vehicles. In manufacturing and improving them epoxy resins can play a major role, if they are adapted accordingly. Combining epoxy resins with polysiloxane block copolymers gets them on the hydrogen track.

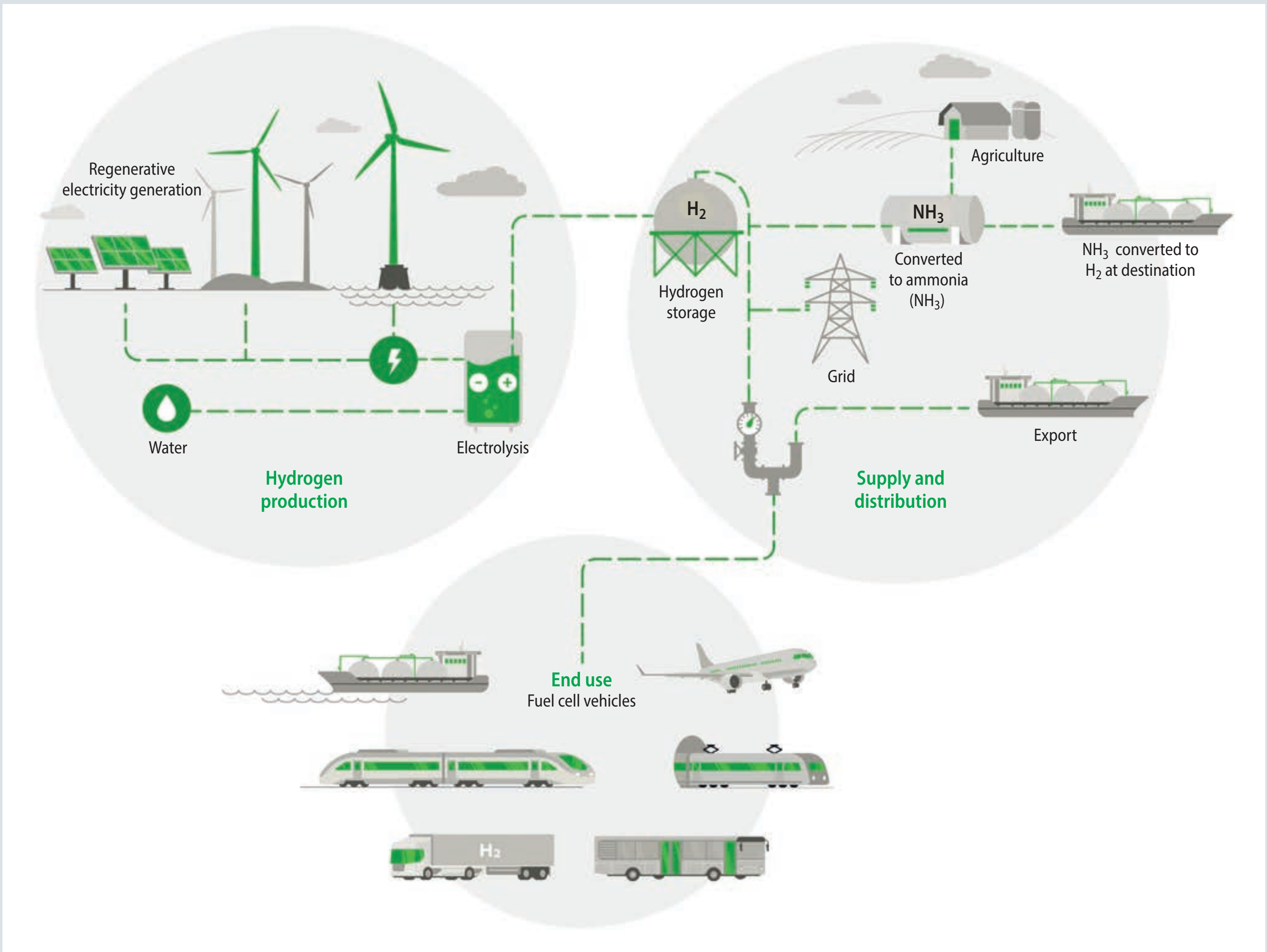

Fig. 1. Green hydrogen can be used as energy source for various means of transportation. Source: Evonik; graphic: © Hanser

Hydrogen will play a major role in the near future, making global transportation significantly more sustainable and independent of fossil resources [1]. In 2023, the market size for green hydrogen was just under EUR 1 billion; by 2030, it is expected to be around EUR 30 billion [2]. This creates new fields of application for existing technologies with very specific challenges. The production of green hydrogen requires electricity from environmentally friendly sources such as wind turbines, hydropower plants or photovoltaics. The hydrogen produced in this way must be stored and transported to the place of use either in gaseous form, cryogenically liquefied or chemically bound. There, the hydrogen is converted into electrical energy using fuel cells, which then drives electric motors (**Fig. 1**).

The use of fuel cell technology and hydrogen in railroad construction is currently being tested and is already showing promising results [3]. While hydrogen

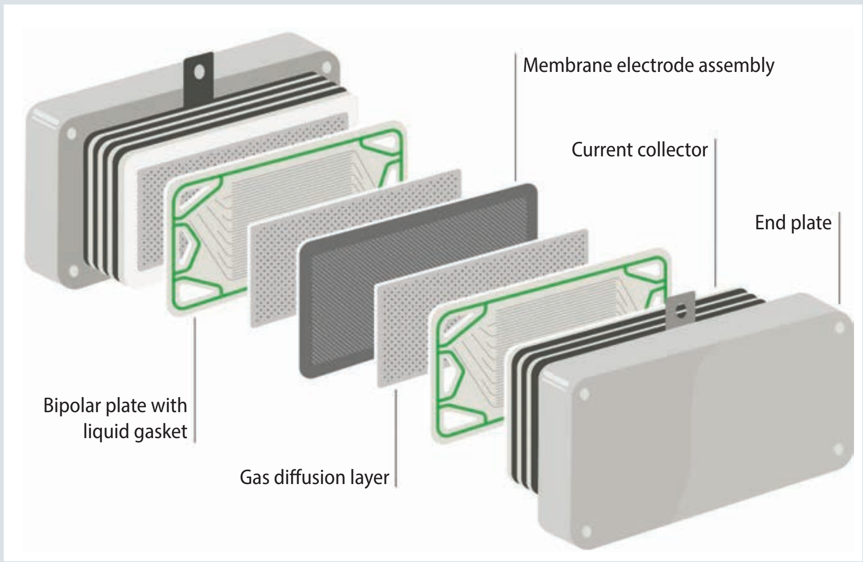

Fig. 2. Schematic structure of an H_2 fuel cell with cured-in-place gasket: the sealant needs to fulfill various requirements. Silicones, polyurethanes and unmodified epoxy resins are not suitable.
Source: Evonik; graphic: © Hanser

propulsion for buses and trucks is already in the second phase of commercialization [4, 5], there are still considerable hurdles to overcome for the use of hydrogen in passenger cars, which make this seem rather unlikely at present. The need to set up hydrogen filling stations throughout the country and the limited tank capacity (and therefore limited vehicle range) due to the low density of hydrogen stand in the way of this.

The potential for hydrogen to power ships is very large. The first prototypes from various shipbuilders are already in use and are being further optimized; intensive research is being carried out on machines, tanks and refueling systems [6, 7]. One particularly elegant solution is the production of hydrogen in offshore wind turbine installations, which can then be used by ships as refueling stations. The costly transportation of electricity by cable to shore is no longer necessary; the hydrogen produced is stored directly on site and does not have to be transported either. The possible use of hydrogen to power aircraft is also currently being intensively investigated, both as a direct turbine fuel and to generate electricity for electric motors [8, 9].

Modified Epoxy Resins in Hydrogen Tanks

In all these applications, hydrogen pressure tanks of different sizes are used; these are usually made of carbon fiber-reinforced composite materials. In a winding process, the carbon fiber strands impregnated with an epoxy resin/hardener mixture are wound around a gas-tight hollow body (liner), e.g. made of PA6 or PA12, and then thermally cured. A variant of this is the so-called Type V tank, which works without a plastic liner.

The challenges for the epoxy resin formulation are particularly high impact strength, even at extremely low temperatures, particularly good fatigue resistance, particularly high pressure resistance and, of course, good gas-tightness against hydrogen. While standard epoxy resin formulations quickly reach their limits here, the required property profile can be achieved by using specially modified epoxy resins. For example, the use of silica nanoparticles can not only increase the pressure resistance, but also significantly improve the fatigue behavior of the fiber-reinforced composite material under cyclic loading [10]. In particular, a combination of classic impact modifiers such as polysiloxane core-shell particles with nanoparticles is already widely used in industry [11].

Optimized Sealant Technology for Fuel Cells

Polymers are used not only in the winding tank, but also in the fuel cell itself, especially as a sealing material (**Fig. 2**). Between the individual components are gaskets used that have to meet special requirements. Prefabricated gaskets made of NBR or EPDM are elastic and gas-tight, but often do not fit precisely and are unsuitable for more complex component geometries. In order to enable fast and efficient fuel cell production, the use of a liquid or paste-like sealing compound that subsequently hardens in the finished component, so-called cured-in-place gaskets (CIPG), is preferred. A flexible sealant with silicone properties is actually preferred; however, the (unfortunately) excellent gas permeability of silicones makes their use difficult. Polyurethanes (PUR) are principally »

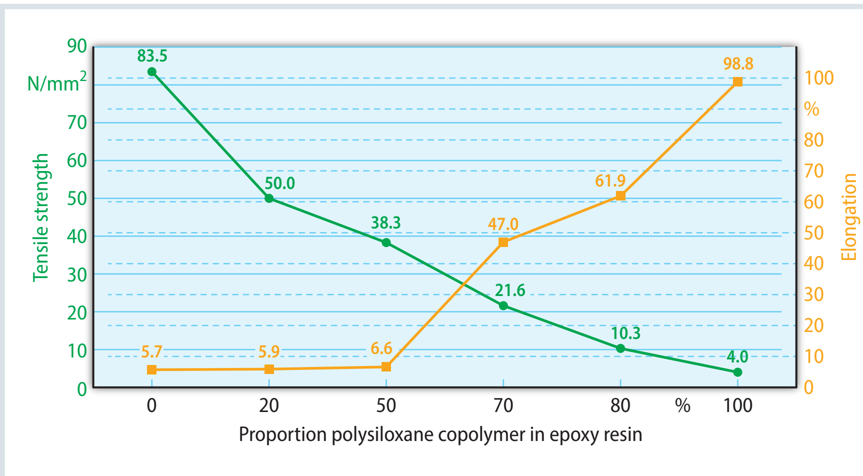

Fig. 3. Tensile strength and elongation as a function of the copolymer addition level: Whereas tensile strength is decreasing with an increasing copolymer addition level, the elongation is increasing. Source: Evonik; graphic: © Hanser

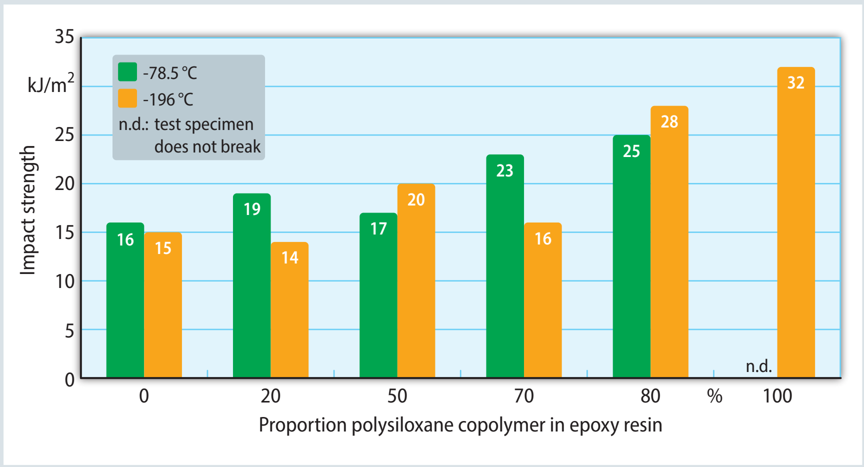

Fig. 4. Impact strength at -78.5 °C and at -196 °C as a function of the copolymer addition level: Toughness is increasing with increasing copolymer addition level. Source: Evonik; graphic: © Hanser

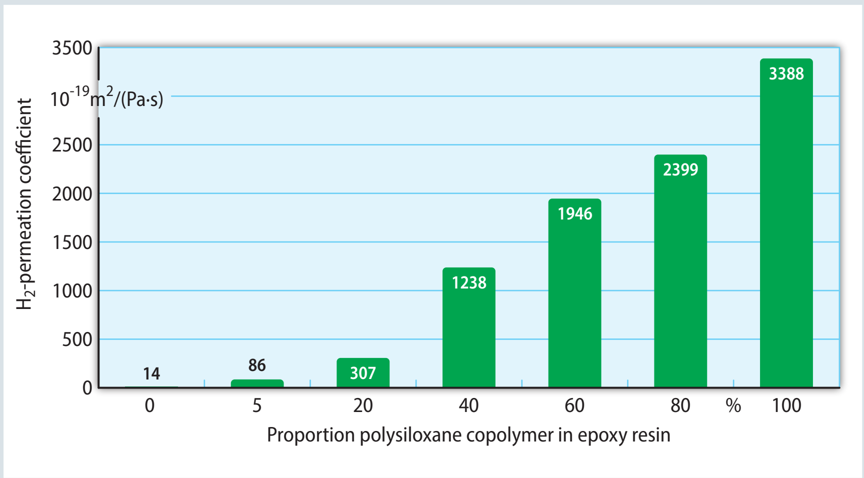

Fig. 5. H_2-permeation coefficient as a function of the copolymer addition level: With increasing addition level the gas permeability increases. Source: Evonik; graphic: © Hanser

suitable as well and show the necessary flexibility; however, their chemical resistance is not optimal.

Epoxy resins seem suitable due to their low gas permeability and particularly good adhesion properties; their chemical resistance is good as well. However, the very high brittleness of standard epoxy resins poses a problem, as the desired flexibility of a seal cannot be achieved. However, if the latest generation of polysiloxane-epoxy block copolymers are used to modify these epoxy resins, highly flexible and resistant systems with very low gas permeability can be formulated. Their low viscosity enables quick and easy processing in production. The desired processing time and curing speed can be determined by the choice of hardener. In addition, the media and aging resistance is further improved compared to standard epoxies – a very welcome side effect of this modification [12].

Are Epoxy Resins Suitable for Sealants?

Investigations by Evonik have shown the achievable property improvements as a function of the amount of block copolymer added. A standard DGEBA resin (comparable to Epikote 828 from Westlake Epoxy) was mixed with varying amounts of Albiflex 297 from Evonik Operations GmbH and cured for 24 hours at room temperature in a steel mold using the stoichiometric amount of Ancamine 2719 (also from Evonik Operations). The viscosities of the mixtures were between 2000 mPas and 20,000 mPas at 25 °C (0 % or 100 % Albiflex 297). The test specimens were then mill-cut or, in the case of the more flexible systems, punched out with a punching knife. To determine the hydrogen permeability, corresponding plates with a thickness of 2 mm were produced in a polytetrafluoroethylene (PTFE) mold.

The tensile test in accordance with DIN 53504 on S2 bars was carried out using a Zwick AllroundLine 20 kN using a pneumatic specimen grip, a long-stroke-extensometer and a 500 N load cell. The 3-point bending tests were also carried out on the ZwickRoell AllroundLine Z020. Flexural strength and flexural modulus were determined in accordance with ISO 178:2019–04.

The Charpy impact strength was determined in accordance with DIN EN ISO 179 using the HIT5P from ZwickRoell (Germany). For the measurement at –78.5 °C, the test specimens were covered with metal sheets on both sides and cooled down to the measurement temperature using dry ice. To determine the impact strength at –196 °C, the test specimens were stored in liquid nitrogen until immediately before the test. The hydrogen permeation measurements were carried out at room temperature using a measurement setup analogous to DIN 53536. In contrast to DIN 53536, however, a gas mixture of 1 bar air and 1 bar hydrogen was used and measured discontinuously until equilibrium was reached.

An important mechanical parameter is the tensile strength of the cross-linked polymer. However, in mechanically fixed components, where tightness plays a significant role, elongation is even more important. In addition, with mechanical stresses such as vibration, impact strength is important. These properties are, of course, required over the entire temperature range; in electric vehicle construction usually –40 °C to +80 °C. When handling hydrogen, in addition to the gas-tightness, which is extremely important for safety reasons, good mechanical properties in the low temperature range are often required.

The Blend Provides the Desired Property Profile

At room temperature, typical strength values for EPDM and NBR are 2 to 20 N/mm^2; with elongations of 100 to 700 %. With silicone formulations, elongations of up to 1000 % can even be realized; however, the achievable strengths are in the range of 1 to 10 N/mm^2. Unmodified epoxy resins have a high strength of 84 N/mm, but have an extremely low elongation of just under 6 % (**Fig. 3**). This is of course completely inadequate for sealing applications. By successive modification with the latest generation of polysiloxane-epoxy copolymers, the elongation can be increased to up to 100 %; however, the strength then decreases accordingly. Depending on the design of the fuel cell, the desired elongation respectively strength can be set via the mixing ratio of epoxy resin/polysiloxane copolymer.

Impact strength is another parameter relating to the mechanical strength of a polymer, but also provides information about fatigue behavior: Under cyclic loading, a higher impact strength generally leads to improved fatigue behavior. Here, too, the impact strength increases significantly both at –78.5 °C and at –196 °C with increasing addition of polysiloxane copolymer – to more than double for the pure copolymer compared to the standard epoxy resin (**Fig. 4**). If other hardeners are used, this difference can be even more pronounced. This applies in particular to anhydride hardeners, which in combination with unmodified epoxy resins generally lead to very hard, brittle thermosets.

As already mentioned, gas tightness against hydrogen is of course another important point. Conventional EPDM gaskets, for example, have values for the H_2-permeation coefficient of 2000 to 5000 x10^{-19} m^2/(Pas), while the value for silicone gaskets is many times higher, at around 50,000 x10^{-19} m^2/(Pas). **Figure 5** shows the corresponding measured values for the formulations with different addition levels of polysiloxane-epoxy copolymer. Although the excellent gas tightness of a pure epoxy resin is lowered somewhat when modified with the copolymer, the values achieved are quite acceptable and comparable with conventional sealing materials and many times better than those of silicones.

Summary and Outlook

Polysiloxane-epoxy block copolymers enable the formulation of liquid and paste-like sealants that crosslink after application in the mounted state. This enables fast (series) production with extremely high fitting accuracy and a low error rate. The property profile can be optimized by choosing the mixing ratio of epoxy resin and copolymer and selecting the hardener: high strength and high flexibility as well as high impact resistance in combination with excellent low-temperature behavior and very good gas-tightness to hydrogen. This promising technology is the subject of extensive developments; work is currently underway on extremely low-viscosity and UV-curable product variants. Intrinsic flame retarded systems with similar performance are also conceivable. ■

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References

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