OPTIMIZED EPOXY RESINS FOR AUTOMOTIVE COMPOSITES: TOUGH, STIFF & FATIGUE RESISTANT

Kumar Kunal, Stephan Sprenger
Evonik Corporation
914 E Randolph Road
Hopewell, VA 23860, USA

Abstract

Lightweight construction is one of the key technologies of the 21st century. Epoxy composites reinforced with carbon or glass fibers are about to replace several automotive parts that were traditionally made using metals. Such composites allow weight reduction and reduced energy consumption in every area of transportation, including automotive, aerospace and shipbuilding. However, the composites manufacturing processes need to be adapted to automotive industry requirements in several ways. For example, automotive applications require epoxy resins with short cure cycles and processes like RTM or wet press process that can easily be automated. Furthermore, the composite materials can be engineered to have the properties demanded by the specific application.

This article presents the capabilities offered by core-shell tougheners and silica nanoparticles to modify epoxy resins for improvements in toughness and stiffness, and also to have outstanding fatigue performance which increases service life. Moreover, the composite parts made with such modified resins have superior surfaces that can be painted right off the mold.

Introduction

Structural epoxy adhesives are used in many automotive applications. As epoxies are inherently brittle, such adhesives are toughened using reactive liquid rubbers or core shell tougheners in order to match the performance needs of the car manufacturer.

More and more automotive parts are made from fiber-reinforced composites. High performance parts are typically produced using glass or carbon fiber-reinforced epoxy materials. Some prominent examples are composite drive shafts, made by filament winding, or composite leaf springs.

The monocoques of formula 1 racing cars and high performance sports cars are already made from composites. Different manufacturing techniques apply. Picture 1 shows the chassis of the Porsche 918 Spyder. The monocoque is made by RTM. The engine compartment however, subject to much higher temperatures, is made from prepregs in an autoclave.
The first attempt towards mass production is made by BMW: the BMW i3 and i8 electrical cars possess a car body which is made by RTM using several different preforms.

Nevertheless, the use of composite in volume car manufacturing faces 2 major issues: the production process needs to become faster (and simpler) in order to match the current cycle times of 1 - 5 minutes. By adapting the curing systems of epoxy resin formulations this can be achieved [2]. The second issue is the epoxy resin performance regarding toughness, strength, fatigue performance, or, in the special case of the leaf springs, compressive strength and creep. By modifying the epoxy resin matrix, these properties can be improved without affecting cure speed or other performance criteria.

Challenges with liquid rubber tougheners

In the mid-eighties of last century, reactive liquid rubbers were introduced as tougheners. Though being very efficient tougheners they have several drawbacks, such as a drop in modulus and Tg of the modified system. These reactive liquid rubbers are blended as adducts with the epoxy resin and phase separate upon cure to form the rubber domains. Since some rubber molecules do not participate in the phase separation but crosslink randomly into the resin matrix, it results in a drop in modulus and the Tg. Furthermore the phase separation happens relatively slowly which does not work very well for high speed cure systems. And, the use of rubber adducts increases the resin viscosity considerably which prohibits their use in infusion processes like RTM, VARTM, ARI etc. where lower viscosities are needed for fast processing.

In this paper two resin modifications will be introduced, which can be combined for ultimate resin performance.

Superior performance with core-shell tougheners

Consequently so-called core shell tougheners have been developed to address the above issues with liquid rubber tougheners. Such materials are available as elastomer particle dispersions with an epoxy-functional particle surface. They have low viscosities, do not lower the Tg and cause a much lower to no reduction in strength and modulus of the modified resin system. Under a microscope the morphology looks identical to an epoxy resin modified with a reactive liquid rubber - as can be seen in Picture 2.
In Figure 1 the toughness increase is compared. It becomes evident that the low viscosity core shell particles are a very efficient toughener and therefore a very suitable raw material for epoxy resin modification for composites manufacturing. And whereas resins modified with reactive liquid rubbers become brittle below approx. -50 °C, epoxy resins modified with core shell elastomers with a polysiloxane core are still tough even below -100 °C [3].

**Figure 1: GIC of DGEBA epoxy resin cured with isophorone diamine**

**Strength and Modulus improvements with surface-modified nanosilica**

For more than 10 years surface-modified silica nanoparticles are available in industrial quantities as concentrates in epoxy resins. They can improve several properties of epoxy resins like strength, modulus, stiffness, compressive strength, reduce creep and increase fatigue performance significantly. They do not increase the viscosity and are therefore suitable for all composites manufacturing methods. Due to their size they can even penetrate close-meshed fabrics. Being transparent, they can be used in exterior parts where the carbon fiber structure is wanted to be visible. In a recent review the relevant improvements of fiber reinforced composites are collected [4]. As an example of property improvement the fatigue performance of a glass fiber-reinforced laminate, e.g. a leaf spring is shown in Figure 2 [5].
Figure 2: Increase in cyclic loadings until failure by resin modification with 10 wt% nanosilica [4]

Toughness and stiffness improvement with hybrid systems

It is found that hybrid epoxy resin systems incorporating both nanosilica and core-shell rubber show outstanding performance compared to unmodified standard resin systems regarding toughness and stiffness [6]. Similar improvements, though of a reduced magnitude, are found when fiber-reinforced composites are made using such hybrid epoxy resins [7].

In Figure 3 an example of a carbon fiber-reinforced composite is given. As can be seen, the addition of nanosilica increases $G_{lc}$ further and reduces the delamination after impact (30 J), thus leading to a tough and stiff laminate.

Figure 3: Fracture toughness and delamination after impact of carbon fiber reinforced laminates
Summary

Epoxy resins used as matrices for automotive composites can be modified using liquid rubber tougheners. However, they present challenges in high viscosity and a drop in Tg and modulus. Such challenges can be overcome with core-shell rubber tougheners. Moreover, a combination of core-shell tougheners and silica nanoparticles can be used to produce composites with

- high toughness and stiffness
- outstanding fatigue performance
- fast curing

Such modifications are very suitable for automotive applications that require high performance and ultrafast curing epoxy systems.

Bibliography

1. Picture source: Porsche AG
6. Sprenger, S. “Epoxy resins modified with elastomers and surface-modified silica nanoparticles” Polymer 2013; 54; 4790 – 4797