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Feature article

Epoxy resins modified with elastomers and surface-modified silica nanoparticles

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ABSTRACT

Epoxy resins are inherently brittle. Thus they are toughened with reactive liquid rubbers or core–shell elastomers. Surface-modified silica nanoparticles, 20 nm in diameter and with a very narrow particle size distribution, are available as concentrates in epoxy resins in industrial quantities since 10 years. Some of the drawbacks of toughening, like lower modulus or a loss in strength can be overcompensated when using nanosilica together with these tougheners. Apparently there exists a synergy as toughness and fatigue performance are increased significantly. In this article the literature published in the last decade is studied with a focus on mechanical properties. Results are compared and the mechanisms responsible for the property improvements are discussed.

1. Introduction

Epoxy resins are used for many years in a multitude of industrial products, like structural automotive adhesives, high performance fibre reinforced composites, electrical and electronic applications, heavy duty protective coatings and many more. However, they are very brittle and therefore in most commercial formulations tougheners are used.

Since the seventies and eighties of last century the use of reactive liquid rubbers as tougheners for epoxy resins became industrial standard. Carboxy terminated butadiene acrylonitrile copolymers (CTBNs) are reacted with an excess of epoxy resin to form a so-called adduct, an epoxy-rubber–epoxy terpolymer. These are soluble in epoxy resins, whereas the pure rubber is not. Upon cure and subsequent formation of the three-dimensional network, the rubber molecules become insoluble again, phase separate and form small rubber domains or particles within the cured polymer matrix. These rubber particles are chemically linked to the polymer. Since the very early work of Kinloch and his team the mechanisms of rubber toughening have been the subject of intensive research and are well understood [1,2].

An excellent review was published recently [3].

However, the phase separation and domain formation depend on the cure speed, cure temperature and the curing agent itself. The acrylonitrile content of the copolymer has an influence on the particle size as well. Furthermore not all long-chain rubber molecules participate in the phase separation, some of them are crosslinked randomly into the epoxy polymer matrix. Consequently the network density is lowered, which results in a lower strength and a lower modulus, and, of course, in a lower glass transition temperature (T_g). Another issue is the relatively high viscosity of epoxy resins containing reactive liquid rubbers which prohibit some applications where low viscosities are required.

To overcome these disadvantages core–shell elastomers (CSRs) have been developed in the 1980s–1990s. Instead of forming a second phase upon cure the rubber particles were added from the beginning. They consist of an elastomeric, rubber-like core of approx. 90 nm; typically a butadiene homopolymer or a butadiene–styrene copolymer with a random copolymer shell of 10–20 nm which is compatible with the epoxy resin [4,5]. They will be referred to as CSR Type I. Others are based on polyacrylate cores and have a diameter in the range of 300–400 nm [6]. They will be referred to as CSR Type II. If these core–shell particles are dispersed in epoxy resins, the viscosities of modified resins are much lower compared to epoxy resins modified with reactive liquid rubbers. The toughening effects are independent from the curing agent and the cure schedule. Sometimes strength and modulus are lowered,

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but not to the same extent as with reactive liquid rubbers. The use in high temperature applications however is limited, as the shell tends to soften at higher temperatures followed by a drastic loss in strength and modulus of the cured polymer.

Another CSR development in the mid-1980s created a material which can be used at elevated temperatures as well [7,8]. This was achieved by reducing the thickness of the shell to a molecular monolayer – the result is rather a core–skin than a core–shell material. These epoxy-functional CSR with a polysiloxane core and an average diameter around 500–700 nm are very efficient tougheners over a very broad range of temperatures [9]. They will be referred to as CSR Type III. Fig. 1 shows the unstained SEM picture of the fracture surface of an anhydride cured epoxy resin containing 5.5 wt% of CSR Type III. The morphology looks very similar to the pictures taken from polymers toughened with reactive liquid rubbers (CTBNs). The rubber domains are very uniform.

In the years 2002/2003 the first commercial grades of surface modified silica nanoparticles were introduced into the market. They are manufactured in situ directly in the epoxy resin by a modified sol–gel process and have an average diameter of 20 nm as well as a very narrow particle diameter distribution.

These particles are completely monodisperse and do increase the resin viscosity only slightly at higher concentrations. In contrast to fumed silica they exhibit no thixotropic properties but behave like a Newtonian liquid. Due to their size they are transparent and can easily penetrate even close meshed fabrics in composite manufacturing when being injected. The property improvements which can be achieved by modifying epoxy resins with these silica nanoparticles, like modulus, toughness and fatigue performance, have been the subject of intensive research in the last decade [10]. The mechanisms how nanoscaled spherical fillers can improve epoxy polymer properties have been identified; however the contribution of each one might be of a different proportion depending on the hardeners used to form the three-dimensional network upon cure. Fig. 2 shows the excellent dispersion and the very narrow particle diameter distribution of the spherical nanosilica.

The combination of reactive liquid rubbers or core–shell elastomers and silica nanoparticles as an additional modifier in epoxy resin systems yields additive and sometimes synergistic property improvements. It becomes possible to formulate tough and stiff materials. Therefore such hybrid systems are used in many industrial epoxy formulations today. The aim of this article is to give a comprehensive overview of the actual state of research regarding the various different aspects and to provide formulation guidelines.

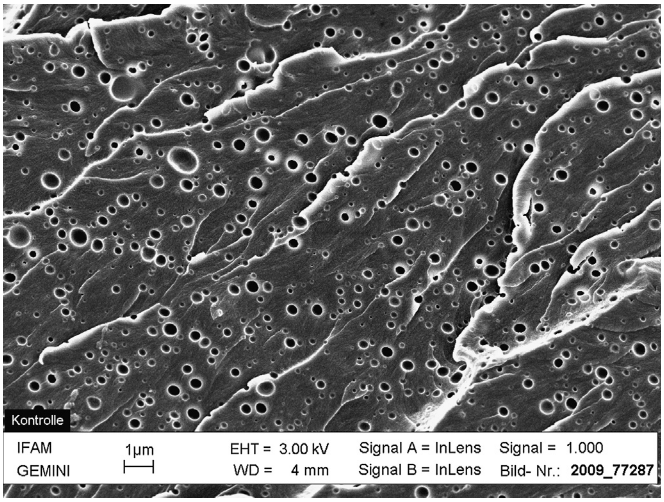

Fig. 1. SEM image of an epoxy polymer with 5.5 wt% CSR Type III.

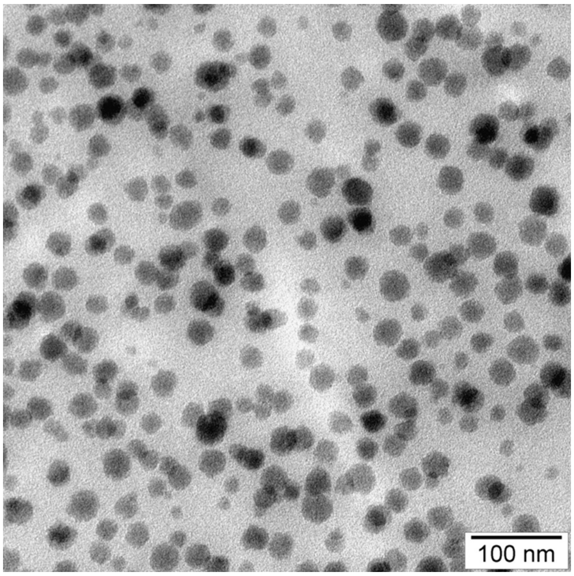

Fig. 2. TEM image of an epoxy polymer with approx. 20 wt% silica nanoparticles [11].

2. Discussion

If not mentioned otherwise, the researchers cited used commercial 40% (by weight) concentrated masterbatches of surface-modified nanosilica in DGEBA from one supplier. These particles have an average diameter of 20 nm and a very narrow particle diameter distribution. They were then diluted down using commercial epoxy resins to vary the nanosilica concentrations.

2.1. Epoxy resins modified with reactive liquid rubbers (CTBNs) and silica nanoparticles, amine cured

The diglycidyl ether of bisphenole A (DGEBA) is the most commonly industrially used epoxy resin. Thus most of the research work was performed using DGEBA.

At first the silica nanoparticles, after being commercially available, had been added to epoxy formulations containing CTBNs to reduce the loss in strength and modulus caused by the rubber modification without increasing the viscosity. Very soon in some applications a synergy between elastomeric tougheners and silica nanoparticles was discovered and patented consequently [12].

However, as will be shown in this article, the synergy is not necessarily related to morphology and sometimes only found for one polymer property or not at all.

One of the first industrial applications where nanosilica was used together with reactive liquid rubbers were structural epoxy adhesives. We found an increase in adhesive lap shear strength at low addition levels of nanosilica (<2 wt%) of a one-component, heat-curing adhesive [13]. The toughness seemed not to be increased further compared to the formulation without nanosilica. This might be due to the fact that the curing agent of this adhesive, dicyandiamide, forms very close-meshed molecular networks. The CTBN rubber in the formulation had 26% acrylonitrile in the copolymer.

In another study we used a rubber with 18% of acrylonitrile and a commercial amine curing agent based on 2,2′-dimethyl-4,4′-methylene-bis(cyclohexyldiamine) and isophorone-diamine. We found that the loss in modulus caused by the rubber modification

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