Carbon fiber-reinforced composites using an epoxy resin matrix modified with reactive liquid rubber and silica nanoparticles

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ABSTRACT

Carbon fiber-reinforced composites are gaining importance and are about to play a very prominent role in automotive applications. In structural applications mainly epoxy resins are used as matrix materials. The properties of epoxy resins and laminates made thereof can be improved by tougheners like reactive liquid rubbers. Further improvements can be achieved by adding surface-modified silica nanoparticles, with 20 nm in size and a very narrow particle size distribution. In this study carbon fiber-reinforced laminates made from epoxy resins modified with reactive liquid rubber and silica nanoparticles have been prepared and investigated. A very fast amine cure of 15 min has been chosen to match industrial needs. Mechanical properties for bulk resins and laminates are compared and the mechanisms responsible for the property improvements are discussed. Structure property relationships between the neat resin fracture toughness and the interlaminar G_{Ic} and G_{IIc} of the reactive liquid rubber and silica nanoparticles modified resins were established. Tough laminates could be prepared. However, CAI performance of the hybrid laminates was slightly inferior as compared to the rubber-toughened laminates, most probably due to agglomerates of nanoparticles found in the cured resin systems. The reason for the nanoparticle aggregation was detected and their influence on laminate performance discussed.

1. Introduction

Environmental requirements like reduced fuel consumption, lower carbon dioxide emission and an improved carbon footprint are changing the automotive industry. Especially in Europe, where carbon dioxide emissions are subject to state regulations [1]. Lightweight construction becomes the key technology to solve these issues which currently drives a trend towards the increased use of fiber-reinforced composites in automotive construction [2].

Automotive could be the third large industrialization of composites technologies, after aerospace and wind energy. In other areas of application like railway or shipbuilding more and more fiber-reinforced materials are used as well. Of course automotive manufacturing has its own rules, one is a very short part production cycle, like the stamping of metal parts. Thus composites manufacturing technologies and the materials used have to be adapted accordingly [3].

Glass or carbon fibers, woven fabrics and unidirectional or multiaxial nonwovens are used as reinforcements; natural fibers are under investigation. Thermoplastic or thermosetting materials are used as matrices. Besides unsaturated polyester resins mainly epoxy resins are used as thermosetting matrices for automotive components. The diglycidylether of bisphenol A (DGEBA) is the most commonly used epoxy resin in automotive industry. Very important is low viscosity of the resin as the preferred manufacturing methods for automotive parts currently are injection or infusion processes – which enable short cycle times [3].

The combination of epoxy resin and hardener defines the matrix material and the various possible combinations enable to formulate according to all possible property requirements [4]. Hare described the variety of epoxy curing agents a few years ago [5,6]. Most popular for automotive part manufacturing are aliphatic or cycloaliphatic amines like isophorone diamine (IPD) due to their low viscosity and fast cure at elevated temperatures. Various accelerators and additives are typically part of the hardener formulation.

However, epoxy resins are inherently brittle. Therefore many epoxy resin formulations are toughened. In the seventies of last century carboxy-terminated nitrile butadienes (CTBNs) were introduced as tougheners. They are immiscible with epoxies but become miscible after a pre-reaction with an excess of epoxy resin. These soluble adducts phase separate again upon cure and form rubber domains in the epoxy resin. The mechanisms of rubber

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toughening are well known [7,8]. Rubber toughening has several drawbacks like lowering the modulus and reducing the glass transition temperature, due to some rubber molecules not participating in the phase separation, but crosslinking randomly into the matrix. Another issue is the relatively high viscosity of epoxy resins containing reactive liquid rubbers, which can be critical for infusion processes. Nevertheless they are used in composites manufacturing.

In 2002/2003 surface modified silica nanoparticles became available in industrial quantities. They are manufactured in situ directly in the epoxy resin by a modified sol–gel process and have an average particle diameter of 20 nm as well as a very narrow particle size distribution [9]. These spherical particles are transparent, monodisperse and just slightly increase the resin viscosity up to quite high addition levels. Resins containing such nanoparticles exhibit no thixotropic properties but behave like Newtonian liquids. The nanosilica does not agglomerate upon cure [9].

Properties like strength, modulus, toughness and especially fatigue performance of cured bulk epoxy resins can be improved by a modification with silica nanoparticles. In 2006 Zhang et al. found significant improvements for an anhydride-cured cycloaliphatic epoxy which was modified with silica nanoparticles [10]. G_{Ic} increased with increasing nanosilica addition level, whereas the impact strength determined by an un notched Charpy test showed a maximum in impact strength at approximately 5 wt% addition level. They studied the correlations between the interparticle distance and the corresponding property improvements and found the improvements for both stiffness and toughness to be larger for addition level where the innerparticle distance became smaller than the particle diameter.

In 1992 Kinloch and Huang postulated that the toughness of modified epoxy resins is the toughness of the unmodified resin plus the contribution of the toughening mechanisms defined by the toughener used [11]. They proposed one of the first models for rubber toughening.

The property improvements achievable with a silica nanoparticle modification and the mechanisms behind have been subject of intensive research in the last ten years [12]. Several toughening mechanisms have been suggested to explain the complex behaviour of polymers with nanofillers, like crack deflection, crack branching, crack pinning/bowing, particle bridging, particle debonding, microcracking or crazing of the matrix and elastic deformation of the matrix. Comparing models with experimental results, Zhang et al. found only a minor contribution to the toughening by crack deflection, but a major contribution by an enhanced local deformability around the crack tip, very probably due to void formation at the crack tip [13].

Today, the mechanisms responsible for the property improvements are rather well understood [14]. Several extensive modelling studies were conducted. Lauke developed a micromechanical model for the toughening of polymers with particles taking into account particle debonding, void formation and subsequent void growth [15]. He concluded that particle size and particle size distribution will both have a very strong influence on toughness improvements achievable with fillers. Williams investigated the toughening from plastic void growth around debonded or cavitated micro- and nanoparticles in epoxy resins [16]. He predicted that smaller particles (<50 nm) will increase toughness more than larger ones but that the improvements only occur when a good particle dispersion can be achieved.

Zappalorto et al. analyzed the debonding-induced toughness improvement from nanoparticle debonding from a polymer using a multiscale model [17]. He concluded that the contribution of matrix debonding to the toughness increase is only a minor one (less than 5%) although necessary for void formation and subsequent plastic yielding.

Kinloch, Taylor et al. studied various epoxy resins cured with different hardeners and different addition levels of nanosilica [18]. They found a good agreement between experimentally measured and predicted values of the fracture energy (G_{Ic}). Their model was based on two major toughening mechanisms: localized plastic shear bands and debonding of silica nanoparticles followed by subsequent plastic void growth.

A multiscale model for toughness increases due to the plastic yielding of voids formed by debonded nanoparticles was developed by Quaresimin et al. [19]. They confirmed that the void growth mechanism provides a major contribution to the toughness increase. Furthermore they were able to show that the toughness improvements depend strongly on nanoparticle size as well. In continuation of this work, Quaresimin et al. investigated a multi-mechanism modelling approach to predict toughness increases of nanoparticle-modified polymers [20]. The major contributions to fracture toughness improvements were described by separate models and then combined: particle debonding, plastic void growth of nanovoids and localized shear banding. The multi-mechanism model shows reasonable agreement with the experimental data.

Due to their size and the only slight increase in viscosity of the resin, nanosilica particles can be used for injection or infusion methods for composite manufacturing where they can penetrate even close meshed fabrics easily. It is well known that properties like modulus, fracture toughness, compressive strength and especially fatigue performance upon cyclic loading can be improved by modifying the epoxy resin matrix with silica nanoparticles. Some properties, e.g. high speed impact performance, were not improved. An extensive review regarding the potential of silica nanoparticles to toughen fiber-reinforced composites was published recently [21].

The combination of reactive liquid rubbers or core shell elastomers and the use of silica nanoparticles as additional modifier in epoxy resin systems yields synergistic property improvements in cured bulk epoxy resins [22]. It is possible to formulate tough and stiff materials. These resin systems and their synergies in various applications, including fiber-reinforced composites were patented consequently at a very early stage [23].

Today such hybrid systems are used in many industrial epoxy formulations. Fig. 1 shows the transmission electron microscopy (TEM) picture of a cured bulk hybrid epoxy resin. Obviously both the rubber particles which have formed upon cure from the reactive liquid rubber and the silica nanoparticles are well dispersed.

Pearson et al. investigated not only the toughening mechanisms but also tried to develop a suitable model to describe them [25]. Based on their results they supposed that the toughening
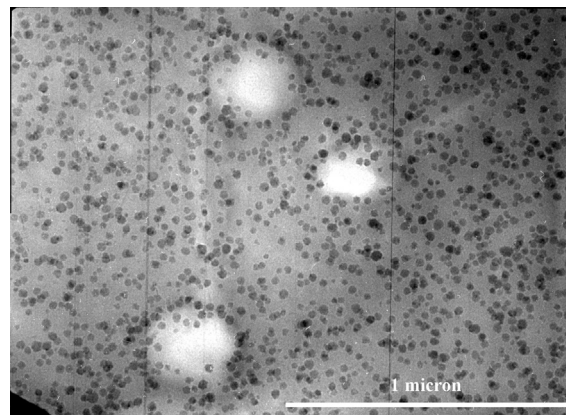

Fig. 1. Transmission electron microscopy (TEM) image of amine-cured hybrid epoxy resin containing reactive liquid rubber (CTBN) and silica nanoparticles [24].