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Quantum dot-based sensor layer in lightweight structures

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ABSTRACT

Quantum dots can be used to detect, store and make visually apparent mechanical loading conditions. The fluorescent properties of the nanocrystals are selectively influenced by the injection of electric charges. By applying an external electric voltage, it is possible to suppress photoluminescence completely. If the quantum dots, as part of a functional layer system, are integrated in smart components, the integrated material system allows for energy-autonomous condition monitoring. We present for the first time a quantum dot-based system in a glass fiber-reinforced epoxy composite with a layer structure which is suitable for impact visualization. The quantum dots dispersed in poly (9-vinylcarbazoles) were applied on a PEDOT:PSS layer on an ITO-coated PET substrate. Silver electrodes were sputtered as a structured layer. For integration of the layer stack, which measured 25 × 25 × 0.1 mm, in an epoxy composite, two process variants and sample geometries were used: a 2D curved component for hand lay-up and a plate for resin transfer molding. The epoxy composite components had a material thickness of 1.5 mm and included eight layers of fiberglass cloth. The quantum dot-layer stacks were positioned either between the first two layers of glass fiber or directly at the component surface which had only a thin epoxy layer. By applying an external voltage, we suppressed the photoluminescence of the integrated quantum dots; the suitability of the coating system for integrated material sensors was evident.

1. Introduction

The energy-efficient design of processes and components is one of the great challenges of today. One method of saving energy is weight reduction by material substitution or optimization. The application of fiber composites has been rising steadily in the automotive industry, the field of aerospace and the manufacture of sports equipment during the last few years. A disadvantage of fiber plastic composites compared with substituted metals is that damage such as matrix cracking or fiber cracks is usually not visible and is undetectable without structural damage. Damage occurs suddenly and without prior plastic deformation. Therefore, it is essential to develop methods for the simple, rapid detection of damage to components with high safety relevance. The known methods for non-destructive monitoring such as ultrasound or computed tomography are complex and require the verification of the complete component, since otherwise localization of damage is not possible. Structural health monitoring (SHM) now offers the opportunity to localize characteristic value deteriorations at any time. Ideally, sensor systems are integrated into the device structure in order to ensure continuous monitoring of components and to protect the sensor system from environmental stresses [1]. Research has focused on a variety of methods for monitoring component states based on various sensor effects and material systems. An overview of current developments is given in [2]. The SHM is a complex system described by a combination of simulation, actuators, sensors, data acquisition and evaluation. In the literature and many research activities only aspects of the complex system are described in detail. An epoxy resin containing carbon nanotubes used to realize a specific electrical conductivity was provided with a grid of contact points. On the assumption, for example, that the electrical conductivity changes locally because of damage, the latter were detected, localized and quantified [3]. Epoxy composites with CNTs or graphene were also the subject of investigations in [4] and [5]. The change in electrical resistance with elastic deformation was considered. The proportion of CNTs in the composite was characterized as an important factor influencing the sensitivity of the method. However, localization of damage is not possible with this method. The combination of fiber Bragg gratings in CRFP and data analysis for the localization of impacts are examined in [6] and [7]. Three main themes that are currently in focus are highlighted: (1) the discrimination between temperature and strain effects, (2) the amplitude spectrum demodulation comprising the measurement of residual stress and (3) the

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connection interface between the embedded sensor and the surroundings. Furthermore, a new monitoring system for rotor blades, consisting of an acoustic emission sensor and embroidered wire sensors for strain measurement that are directly integrated in the device structure, has been described [8,9]. Another general approach is the use of quantum dot-based sensor systems. In comparison with organic fluorescent compounds the fluorescence of quantum dots can be electrically quenched. This approach simplifies the monitoring of lightweight structures which need regular inspection, such as automotive parts or cycling helmets.

This paper focuses on the development of a functional quantum dot layer system which visualizes mechanical impact by quenching photoluminescence. Therefore it can be used in the field of structural health monitoring [10,11]. Charges from an external source are transferred to quantum dots which cause photoluminescence quenching. If the charges are stored temporarily, loading conditions of lightweight structures will be visually recognized and measured. Hence damaged lightweight structures can be replaced in time. In this paper the preparation of a quantum dot sensor system and its performance inside the lightweight structure are demonstrated.

2. Materials and methods

2.1. Processing of functional layer stacks

The functional layer systems were fabricated by spin-coating on pre-cleaned PET-ITO substrates with a size of 2.5 cm × 2.5 cm. PET-ITO substrates and poly(vinylcarbazole) (PVK) were purchased from Aldrich. PEDOT:PSS was also supplied by Aldrich and applied as a charge transport layer. Core shell-type quantum dots, dispersed in toluene (CdSe/ZnS; emission wavelength 610 nm, 5 mg/mL) were obtained from CAN Hamburg.

PEDOT:PSS dispersion in water diluted with ethanol in a volume ratio of v/v = 1/2. 200 μL was spin-coated 3 times on a pre-cleaned substrate. The best film properties were realized at 3000 rpm and a spin-coating time of 25 s. After the first and second layer the film was annealed for 5 min at 100 °C. After deposition of the third layer the PEDOT:PSS coated substrate was dried for 1 h at 110 °C.

Quantum dot dispersions (5 mg/mL in toluene) were mixed with PVK, which was also dispersed in toluene beforehand. Therefore, 20.6 mg of PVK was dispersed in 1 mL of toluene and used as a matrix material for quantum dots. The QD/PVK mixture consisted of 1 mL of QD dispersion and 0.5 mL of PVK dispersion and was spin-coated at 1000 rpm for up to 25 s. After deposition of 150 μL of PVK/QD-mixture by spin-coating the layer stack was dried for 15 min at 95 °C. On top of the layer stack aluminium was deposited by sputtering technology having a thickness of 100 nm.

EPO-TEK 301-2 supplied by Epoxy Technology Inc., USA and 25 g/m^2 Panda™ plain weave glass fabric distributed by R&G Faserverbundwerkstoffe GmbH, Germany were used for the glass fiber/epoxy laminate. The epoxy resin was specified by the manufacturer to have a spectral transmission of >94% @ 320 nm, >99% @ 400–1200 nm, >98% @ is 1200–1600 nm (see Table 1).

2.2. Integration of functional layer stacks into lightweight structures

Before the embedding of quantum dot layer systems, the ITO electrode and the aluminum electrode were connected with polymer-coated copper wires; the polymer coating was to prevent a shortcut of the wires in case of contact. An epoxy resin containing silver was used for the glass fiber-epoxy laminate.

Afterwards the prepared functional layer stack was embedded into an epoxy resin/glass-fiber-reinforced composite structure.

Table 1
Materials for transmittance test.

Material	Description
Cloth 1	Glass fabric 49 g/m^2 (Finish FE 800, plain); R&G GmbH, Germany
Cloth 2	Glass fabric 25 g/m^2 Panda™ (plain weave); R&G GmbH, Germany
Epoxy resin 1	Epoxy resin L (bisphenol A/F epoxy resin); R&G GmbH, Germany
Epoxy resin 2	EPO-TEK 301-2 (bisphenol A) epoxy resin, Epoxy Technology Inc., USA
PET-ITO substrate	Aldrich

Previously the transmission behavior of the cloth and the epoxy resin was characterized by UV/VIS measurements to ensure optical transparency in the photoluminescent region of the quantum dots. The integration resulted in plane samples for resin transfer molding (RTM) and 2D curved samples for hand lay-up, a laboratory method (right, plane sample) (Fig. 1). RTM was chosen to prove the performance of the quantum dot layer in components manufactured by an established technology for medium volume production [12].

The quantum dot functional layer stack was positioned between the glass fiber plies in the two-part tool before epoxy resin was injected into the mold. A symmetric isotropic layer construction of the structural part with a fiber volume fraction of 50% was applied for the integration of a quantum dot layer system. The reinforcement was realized by a glass fiber fabric using both a twill weave of 2/2 with a basic weight of 282 g/m^2 and a Panda™ plain weave glass fabric with a basic weight of 25 g/m^2. The matrix system was composed either of epoxy resin L (Bisphenol A/F) and hardener EPH 294 at the mass ratio of 100:31 or epoxy resin EPO-TEK 301-2 (Bisphenol A) part A and part B at the mass ratio of 100:35.

Resin transfer molding (RTM) acted as manufacturing process for the plane panels (size: 510 mm × 680 mm × 1 mm). After filling of the tool, the maximum pressure was gradually adjusted in the following order: 5 min at 1 bar, 2 bar till the complete filling, 20 min at 3 bar. The mold was heated during the filling to 60 °C in order to reduce the viscosity of the matrix resin. As a result the wetting behavior of the glass fiber layers was improved and the amount of gas bubble content and air pockets reduced. The part was cooled down in the mold afterwards. Finally, the component was cured and demolded. The panels were cut into samples measuring 50 mm × 50 mm and the quantum dot layer system was electrically connected for upcoming characterization.

Another method for processing reactive casting resins is the *hand lay-up*. This simple procedure, well-suited for the laboratory, was applied during the preparation of the above-mentioned 2D structure. First, the mold surface was provided with a release agent and a gel coat, which prevented the fiber structure being drawn to the outside and protected the tool. Thereafter, epoxy resin and glass fiber layers were applied to the tool surface one after another. The QD films were positioned between the fiber glass layers. For mechanical reasons the layer stack was introduced beneath the first glass fiber. The infilling of the resin in the individual fiber layers was realized with a wet-on-wet brush or roller. The tool consisted of two halves in order to guarantee the same quality on the surface of the top and bottom of the composite. After being cured at room temperature for 48 h, samples were cut out of the structure and contacted electrically.

2.3. Methods for characterization of functional layer stacks

The quantum dot distribution was investigated by fluorescent microscopy (Olympus IX-51). The quenching behavior was