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Nanoparticle reinforced epoxy gelcoats for fiber-plastic composites under multiple load

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ABSTRACT

Novel surface coatings that are load-adapted and suitable for economical manufacturing are required for fiber-plastic composites subjected to complex loads. They must have good wear and chemical resistance compared to conventional thermoset coatings (paints, gelcoats), and high failure strain and adhesive strength compared to metallic or ceramic protection layers. Polymeric nanocomposites offer particular advantages in this respect. Given this background, the main aim of this work is to characterize and evaluate surface-protection layers made of metal oxide nanoparticle reinforced epoxy gelcoats for mechanical, tribological and media loaded fiber-reinforced plastics (FRP). The focus is set on the property characterization of the heterogeneous gelcoat as a function of particle material and filler content, as well as the adjustment of the required rheological properties of the liquid particle-resin dispersion so that nanoparticle reinforced gelcoats can be applied to the anisotropic FRP substrate by spray processing in an economical and variable-geometry manner.

1. Introduction

The use of conventional coating processes to apply functional surface layers on components made of fiber-reinforced plastic (FRP) is often prevented by many technological and material-based factors. These include limited process temperatures due to the low thermal stability of the polymer matrix, low or inhomogeneous electrical conductivity and a non-uniform fiber-matrix surface of the FRP structure. The application of homogeneous and adherent functional layers on highly stressed FRP components is therefore associated with high process-related efforts (e.g. [1–4]). Previous developments for application of functional coatings on fiber-plastic composites are limited to hybrid constructions in which the stressed zones are substituted by metal components as well as specific coating processes for simple part geometries (see Fig. 1).

According to the state of the art hard and wear-resistant metal or ceramic layers can be applied on FRP structures using thermal spray technique, but usually require large rework and offer only a small failure strain, which is significantly limiting the range of applications (cp. [5,6]). Also PVD/CVD processes are suitable to deposit diverse metals, ceramics and organic hard materials with relatively high strength, adhesion and failure strain on fiber-plastic composites. However, the thin film thickness of such coatings protects the FRP substrate only at low tribological and corrosive conditions (e.g. [7]). The electroless deposition on FRP structures, in particular of NiP layers, offers a higher protection against wear and diffusion compared to thin-film technologies and at the same time sufficient coating toughness, but requires high process efforts to obtain homogenous, dense and adherent surface layers (cp. [8]).

In order to counteract the disadvantages of conventional coating materials and completely exploit the lightweight potential of continuous-fiber reinforced plastics, novel functional layers with matched mechanical behavior of materials and high adhesive strength on the one hand and sufficient wear and moisture resistance on the other side are needed. According to this, special benefits are offered by inorganic-organic surface layers based on polymer nanocomposites. Due to the introduction of hard metallic or ceramic nanoparticles (<100 nm) in polymeric matrices hardness, strength, modulus and wear resistance of the plastic material can be increased substantially and adapted to the often complex requirements (cp. [9–12]). The nanoscale reinforcement occurs in strong interaction with the polymer based on the large specific particle surface, so that small degrees of filler content will lead to large changes in the material properties. Due to the particle size in the nanometer range also the failure strain of the polymer increases related to particle material, filler contend and quality of the dispersing process (e.g. [13,14]).

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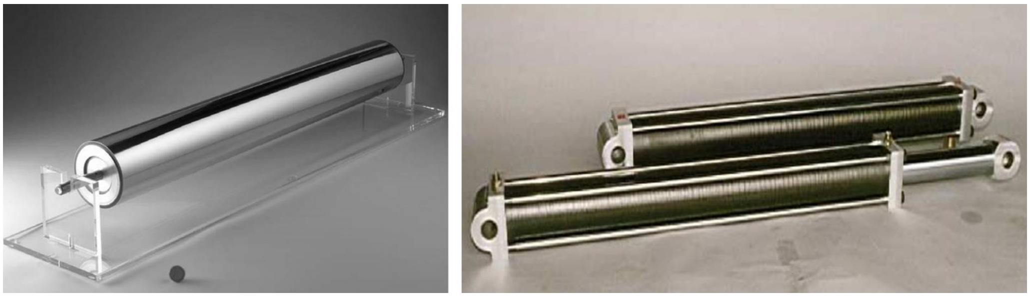

Fig. 1. Examples of FRP components with functional surface layers: electroless metallized light-weight print roller (left) and CFRP hydraulic actuator with an internal steel liner (right).

The high potential of polymeric nanocomposites, in particular in terms of hardness, stiffness, strength, wear resistance and barrier properties, compared to non-reinforced plastics could be demonstrated in numerous scientific papers, whereby the focus is on the characterization of the specific properties of the nanocomposite material itself (cp. [9,10,13–16]). The use of thermoset nanocomposites as a functional surface layer is used both to increase the barrier against moisture diffusion using platelet-shaped organoclay [17,18] as well as to increase the abrasion resistance and conservation of surface gloss of paints by means of spherical nanoparticles [19,20]. In some publications, epoxy and unsaturated polyester resins with incorporated nanoparticles for use as wear-optimized surface layer are described. Here, a higher resistance to abrasive wear and increased weather resistance can be achieved due to finely dispersed metallic oxide nanoparticles (cp. [21–23]). However, such nanocomposite layers are confined mainly to metallic substrates.

A comprehensive investigation of polymer nanocomposites for use as a gelcoat for tribological, mechanical and hygric loaded fiber-plastic composites is still missing. Not only the type of application and the layer-substrate adhesion mechanisms differ fundamentally with respect to metallic substrate materials, but also the inherent properties of the surface layer due to different film formation processes and stresses. In this context, comprehensive studies on the characterization and evaluation of epoxy-based nanocomposites as a functional layer on complex stressed CFRP substrates provide the focus of this work.

2. Materials and tests

The experimental analyses are accomplished on particle-resin composites using spherical metallic oxide nano-fillers based on untreated (SiO_2) and with hexamethyldisilazane surface-modified fumed silica (SiO_2(mod)), titanium dioxide (TiO_2) and aluminum oxide (Al_2O_3) (see also Table 1). SiO_2(thix) are surface-modified fumed silica particles with high thixotropic properties to adjust the rheological behavior of the epoxy-particle mixture. The nanoparticles are present in powder form and were introduced finely dispersed into an anhydride-curable epoxy resin system in the filler contents of 0.5, 1, 2, 4 and 6 vol%. The homogeneous dispersion of the selected nanoparticles has been done using a 1 kW lab dissolver (Type: DB13, Co.: Techo GmbH) under vacuum conditions. The epoxy system consists of Araldite 556 (resin), Aradur 906 (hardener) and DY 070 (accelerator) with a mixing ratio of 100:95:1 parts per weight.

The homogenized nanoparticle-resin dispersions are processed both by the spray process for the production of surface layers on flat textile-reinforced epoxy laminates as well as for manufacturing samples made of substrate-free molding material. The nanocomposite molding material ensures standardized testing of mechanical, tribological and medial properties of the film material without disturbing influence of the substrate. In attempts to characterize the specific surface layer properties of the nanocomposite, gelcoat-substrate specimens are used (see Fig. 2).

For manufacturing of these multilayered specimens the same epoxy matrix is used for the gelcoat as well as for the FRP structure. The substrate consists of a carbon fiber laminate of individual UD layers (320 g/m^2) having a structure of $(0/90/0/90)_s$ and a laminate thickness of 2 mm. The gelcoat was applied with an averaged film thickness of 0.3 mm on both polished surfaces of a planar and rectangular stainless steel mold by conventional compressed air spray technique. This requires an adjustment of the rheological properties of the particle-resin dispersions to obtain the required intrinsic viscosity and the low fluid viscosity during the spraying process. After reaching the gel point under elevated mold temperatures of 80 °C the UD layers were placed inside the mold containing the pre-crosslinked gelcoat and resin impregnated by conventional hand lay-up method. The curing and complete crosslinking of both the CFRP substrate and the gelcoat takes place in a heated press under 5 bar pressure at 120 °C and 160 °C for two hours each. This curing cycle leads to a glass transition temperature of 165–170 °C [24].

To manufacture specimens of pure nanocomposite molding material the liquid particle-resin dispersion was filled into a planar and rectangular polished stainless steel mold with a cavity height of 4 mm and then cured in the same way: 120 °C and 160 °C for two hours each. Flat samples in different geometries depending on the test procedure were cut out of the flat plate by water jet.

Within the scope of this work, the mechanical, tribological and hygric material properties of the epoxy-based nanocomposites as well as the rheological properties of the particle-resin dispersions will be characterized as a function of particle material and filler content. This requires extensive experimental investigations on the selected nanocomposites (see also Table 2):

- Mechanical characterization of the nanocomposite as pure molding material and as gelcoat on the CFRP substrate.
- Analysis of the friction and wear behavior at frictional load.
- Determination of the diffusion properties during one-sided wetting by water.
- Rheological investigation and adjustment of the viscosity behavior of nanoparticle-modified epoxy dispersions as a function of shear rate and temperature.

3. Experimental results and evaluation

3.1. Rheological properties

The application of polymeric nanocomposites to form a homogeneous defect-free surface layer in the FRP structures using spraying technology necessarily requires a modification of the rheological properties of the particle-resin dispersion. Most particle materials with reinforcing effects have no influence on the intrinsic