Available online at www.sciencedirect.com
ScienceDirect
Composites Science and Technology 68 (2008) 2892–2901
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Nanocomposite coatings for healing surface defects of glass fibers and improving interfacial adhesion

Shang-Lin Gao, Edith Mäder *, Rosemarie Plonka

Leibniz Institute of Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany

Received 20 September 2007; accepted 15 October 2007
Available online 23 October 2007

Abstract

Surface defects of brittle materials cause actual tensile strength much lower than the ultimate theoretical strength. Coatings can be used to 'heal' surface flaws and modify surface properties. Here, we describe an online process by which a nanometer-scale hybrid coating layer based on styrene-butadiene copolymer with single or multi-walled carbon nanotubes (SWCNTs, MWCNTs) and/or nanoclays, as mechanical enhancement and environmental barrier layer, is applied to alkali-resistant glass (ARG) and E-glass fibers. Our data indicates that the nanostructured and functionalised traditional glass fibers show significantly improved both mechanical properties and environmental corrosion resistance. With low fraction of nanotubes in sizing, the tensile and bending strength of healed glass fiber increases remarkably. No apparent strength variation appears for nanoclay coated fiber subjected to alkaline attack. We introduce a healing efficiency factor and conclude that the coating modulus, thickness and roughness are responsible for the mechanical improvement of fibers. Besides, nanocomposite coatings result in enhanced fiber/matrix interfacial adhesion, indicating nanotube related interfacial toughening mechanisms.

Keywords: A. Coating; A. Glass fibers; A. Nanostructures; A. Nanocomposites; B. Surface treatments; B. Strength; B. Interfacial strength; C. Crack Fiber bridging; D. Atomic force microscopy (AFM)

1. Introduction

Most solid materials have surface defects. For glass and other brittle materials, surface defects cause the measured mechanical properties significantly lower than their theoretical values. The nanoscale surface defects providing extra stress at the tip of the cracks can lead to stress-corrosion cracking at low stress level, particularly in a humid environment. Our recent work showed that the surface critical flaws have size in a range of a few hundred nanometres which encouraged us to investigate whether the nano-reinforcements with similar size functions as a crucial role for healing [1,2]. Healing nanoscale surface flaws and enhancing materials' lifetime by nanocoatings, therefore, are important for many traditional materials.

Reinforcement with nanomaterials is a topic of significant current interest. It is well-known that surface defect-free and high purity carbon nanotubes have exceptional high Young's modulus and tensile strength. However, an efficient utilization of the excellent properties of nano-reinforcements to the microscopic and macroscopic level is a long standing problem. To date, the highest strength and Young's modulus reported in the literature are relatively disappointing: 1.8–3.2 GPa and ~40 GPa, respectively, for aligned nanotube composite bundles with very high volume loading of nanotubes (60 wt%) [3,4], which are a factor of ten below those of the component individual nanotubes because of poor integration and weak interfacial adhesion. Therefore, to find an appropriate dispersion for the nano-reinforcements to increase volume concentration, limited by chemical inertness and van der Waals

* Corresponding author. Tel.: +49 0351 4658 305; fax: +49 0351 4658 362.
E-mail address: emaeder@ipfdd.de (E. Mäder).

0266-3538/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2007.10.009

attractions, is not sufficient for producing high-quality composites. In contrast to this 'super-materials degraded by defects' approach, here, we apply a 'surface defects healed by super-materials' approach (Fig. 1), where the traditional alkali-resistant glass fibers (ARG) were coated using different nanostructured coating layers with low loading (<1 wt%) of single and multi walled carbon nanotubes (SWCNTs, MWCNTs) and/or organoclay to provide a protective layer against aqueous alkaline solution. AFM, SEM, TEM and single fiber tensile, bending and pull-out tests were used to investigate in detail the local surface topography, mechanical and interfacial properties.

2. Experimental

2.1. Materials

The control ARG with diameter of 17 μm and E-glass fibers with diameter of 20–23 μm utilized in this work were made at our institute. During the continuous spinning process, the ARG fibers were in situ sized by an alkali-resistant sizing consisting of silane coupling agent, γ-aminopropyltriethoxysilane, in conjunction with film formers in the aqueous sizing, namely S1. Additionally, either MWCNTs or nanoclay particles are dispersed in the epoxy film former based sizing. The 0.2 wt% surface functionalized MWCNTs in the sizing were synthesized by an arc-discharge method (IFW, Germany) with an external diameter of 20–60 nm and a length of 100–1000 nm as described in Refs. [5,6]. We applied additionally surface coatings to the control ARG using a commercial self-crosslinking styrene-butadiene copolymers (C2). The total weight gain due to the coatings is 5.3 wt% measured by pyrolysis (600 °C, 60 min) of the coated fibers. The 1 wt% organically modified silicates on the base of montmorillonite particles with a size of about 60–300 nm (Nanofil 15, Süd-Chemie AG, Moosburg, Germany) are dispersed in the obtained solution. A quaternary ammonium surfactant and a non-ionic surface active agent were added to the dispersion for homogeneous distribution of the constituents. We extracted the fibers in selected highly concentrated aqueous alkaline solution (5 wt% NaOH, pH of 14) at 20 °C for seven days, which is the most aggressive and corrosive condition to the fiber surface [1].

The E-glass fibers were also sized with aminosilane and maleic anhydride grafted PP film former dispersion containing less than 0.5 wt% nanotubes in the sizings. Simultaneously, thermoplastic polypropylene filaments with diameter of 26 μm are manufactured from homopolymer PP (HD120M) and 2% Exxelor PO 1020 acts as the compatibiliser to improve the adhesion strength of the commingled yarns. This method of concentrating the nanomaterials in the sizing dispersion benefits from its ambient temperature treatment and environmentally friendly deposition, in addition to chemical versatility.

2.2. Characterization

2.2.1. Atomic force microscopy (AFM)

An AFM (a Digital Instruments D3100, USA) was used as a surface morphology imaging tool to detect fiber, coatings and fracture surfaces. The topography and phase images of samples were studied in tapping mode, while phase shifts, i.e., changes in the phase angle of vibration with respect to the phase angle of the freely oscillating cantilever, recorded simultaneously with height changes, are present as a phase image. Its value depends on the energy dissipated in the tapping interaction of probe and specimen, which is normally sensitive to the surface and underlying structure of the specimens that could not be observed in the topography image due to variations in local elasticity and viscoelasticity, adhesion, hydrophilicity/hydrophobicity properties of the specimen [7–9]. The phase images reveal differences in these surface properties of the material which are currently only qualitative in nature. The cantilever (ULTRASHARP NSC16/50, MikroMasch, Estonia) has a normal spring constant of 35 N/m, a tip cone angle of 20°, radius of 5–10 nm and modulus of 160 GPa to

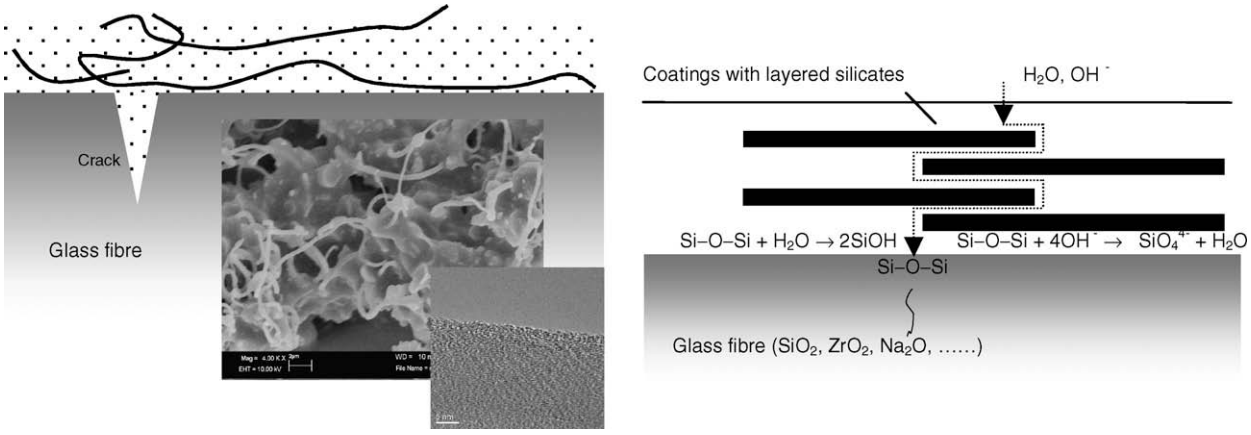

Fig. 1. Schematics of nanostructured coatings with nanotube/layered silicate polymer network on glass fiber surface to enhance flaw healing effect and corrosion resistance. The inserts show polymer/MWCNT network by SEM and individual surface functionalized nanotube structure by TEM.