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Interphase modification of alkali-resistant glass fibres and carbon fibres for textile reinforced concrete I: Fibre properties and durability

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ABSTRACT

Sizings and coatings are considered to heal severe surface flaws of brittle alkali-resistant glass (ARG) fibres. The interaction between sizings and coatings is varied systematically resulting in different surface modifications and interphase properties in cement matrix composites. Investigations of the durability after accelerated aging are made and the mechanical properties of sized and coated ARG are elucidated as a function of fibre diameter, sizing and coating content, respectively, as well as their chemical formulations under special consideration of nanotubes and nanoclay concentrated within the interphase. Furthermore, the results achieved with nano-dispersed polymer coatings on glass fibres are transferred to carbon fibres.

1. Introduction

Textile reinforced concrete (TRC) is a rather new family of composite materials which aging behaviour during long-term exposure to alkaline environments is relatively unknown at present. For alkali-resistant glass fibres multifunctional sizings and coatings are required for both structural stabilisation of textile fabrics to ensure well aligned reinforcement in concrete parts and improvement of fibres performance, particularly the surface protection, abrasion resistance, strength maintenance and especially interphase formation in the composite [1,2]. The alkali-resistant glass fibre (ARG) was preferably designed to reinforce cementitious matrices which have been widely used in construction and civil engineering. Under the strong conditions in cementitious environment (pH-value > 12.5) glass fibres (even AR-glass fibres) are not completely inert. The chemical reactions on the glass fibre surface can be roughly summarized in the following equations:

$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-+\mathrm{OH}^{-} \rightarrow -\mathrm{Si}-\mathrm{OH}+-\mathrm{Si}-\mathrm{O}^{-} \quad (1)$$

$$-\mathrm{Si}-\mathrm{O}-+\mathrm{H}_2\mathrm{O} \rightarrow -\mathrm{Si}-\mathrm{OH}+\mathrm{OH}^{-} \quad (2)$$

The non-bridging oxygen formed in reaction Eq. (1) interacts with a further molecule of water producing a hydroxyl ion Eq. (2), which is free to repeat reaction Eq. (1) [3]. The corrosion process in alkaline solutions is mainly determined by the break up of the glass forming –Si–O–Si– bonds leading to a completely destroyed network. However, it has been reported that for improving long-term performance of glass fibre-reinforced concrete, it is very important to develop new types of coatings to modify the ARG fibre surface and improve their durability [4]. Furthermore, it was examined, how the coatings on glass but also on carbon fibres interact with the surrounding cementitious matrix for the improvement of the composite performance [5]. The sizing on commercial ARG, which is typically a few tens of nanometer of average thickness, basically consists of components of an organo silane coupling agent, a polymeric film former and a lubricant, leading to variable properties and great difficulty in both process control and insitu characterization, because its formulation is unknown. Therefore, little has been solidly established about the mechanical properties, morphology and exact corrosion mechanisms of the polymer coatings and/or fibre surface layer in various environmental conditions. Model formulations of sizings and coatings containing small amounts of multi-walled carbon nanotubes (MWNT) and montmorrilonite (MMT, nanoclay) have been applied to virgin ARG in order to gain comprehensive insight into what mechanisms are responsible for variation of fibre tensile strength [6,7]. The mechanical property improvement by reducing the fibre surface flaw formation and crack growth requires the consideration of potential mechanisms including the contributions of different factors. Note that the polymer coatings have Young's moduli that are typically several orders of magnitude lower than the glass fibre, and therefore do not bear a significant portion of the mechanical load. Although the polymer coatings do not increase strength, they have the important function of protecting

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the glass surface from abrasion and chemical damage, which in turn would degrade glass fibre strength. The coating layer with organosilicate plates could additionally prevent moisture/alkali contact and reaction with glass lattice at a crack tip (stress corrosion). The coating is effective in several ways, firstly, the acidic groups of coating molecularly interact with or absorb free cations and anions of environment leading to a slow-down of the corrosion process. Secondly, stress-redistribution and crack stopping mechanisms by coatings and nanotube's 'bridging' effect and interface debonding/plastic deformation around crack tip could occur. The mechanical 'healing' effect was viewed as a disappearance of the severe surface flaws because of an increase of the crack tip radius, the flaw partly filled by coatings being either elliptical than sharp. Thirdly, compressive stress on fibre surface might prevent crack opening/propagation by the shrinkage of polymer due to solidification. As schematically shown in Fig. 1, solidification of coating polymers is accompanied by shrinkage as liquid evaporation (solvent removal) and curing (chemical reaction) occurs, which generates a tensile stress within the polymer layer and a compressive stress towards the surface of substrate. Because of the compression closing surface flaw, the strengthening can be increased by increasing the magnitude of the compressive stress [8]. Stress development in drying coatings and explanations for the different stress levels measured for the various polymers can be found elsewhere [9]. Throughout most of a coating, the stress is solely in-plane tensile stress, at edges and inclusions of nanoparticles, more complex concentrations of stress arise and its effect on the efficiency of flaw healing need further investigation.

To simplify the complex phenomena, a simple mechanical model based on Griffith fracture mechanics was developed to roughly estimate the strength of a coated fibre, as described in detail elsewhere [10]. Based on this approach, a smoothly coated fibre is considered to be loaded in tension and having a thin circumferential crack (Fig. 2). When the crack appears, the strain energy is released in a material volume which comprises a conical ring whose generating lines are shown by broken lines and heights are proportional to the crack length. This assumption is arbitrary and significant analogy to the original Griffith strain energy analysis for an elliptical, sharp crack embedded in a flat, brittle sheet [11] without consideration of surface coatings [12].

The coating is a widespread method of providing corrosion protection in order to improve the processing behaviour and the durability of engineering structures. Water is the major cause of swelling, loss of adhesion, deterioration of mechanical properties and the start of the corrosion process. It was widely recognized that polymer–nanoclay composites, made by intercalating organophilic montmorillonite to interpenetrating different polymer networks, have excellent barrier capability with significantly reduced permeability to moisture and gases [13,14]. The moisture permeability and diffusion behaviours of nanocomposites normally depend on the polymer type, nanoclay content, aspect ratio and degree of dispersion on silicate layers, as well as the interfacial adhesion. It was found that the water diffusivity in general decreased with increasing clay content and was reduced to half of its value in the neat vinylester resin with only 1 wt% of clay and the water absorption rate was reduced by about 40% for nanoclay–polyamide composites compared with the neat polymer [15]. A 50–80% decrease in water absorption was also reported for epoxy and poly(ε-caprolactone) nanoclay composites [16,17]. A combined experimental and theoretical study of various poly(ethyleneoxide)- and poly(propylene oxide)-based compounds intercalated in montmorillonite and hectorite clays was studied and the diffusion coefficient of water molecules was reported as 4–32$\cdot 10^{-8}$ cm^2/s [18,19].

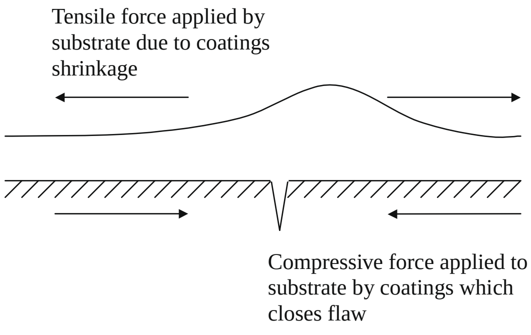

Fig. 1. Schematic solidification of coating polymers accompanied by shrinkage on glass fibre with a surface flaw.

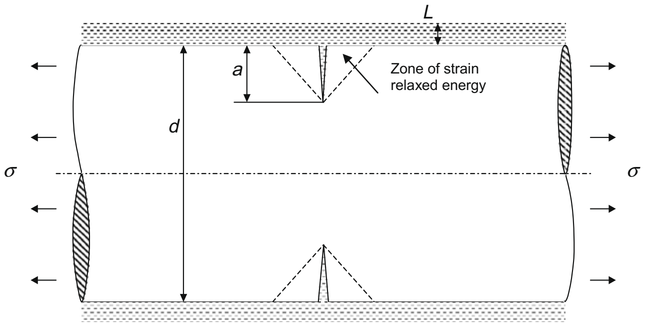

Fig. 2. A sketch of a coated fibre with a surface flaw. The fibre is loaded in tensile stress σ and the circumferential surface flaw of length a serves as an initial crack. The fibre diameter and coating thickness are given by d and L, respectively, where a and L are much less than d.

One of the most impressive strengthening methods for structural concrete is the use of carbon fibres, because of their high mechanical properties and high alkali-resistance due to chemical inertness of carbon. The limiting parameter in a cementitious carbon fibre composite is the bond between the fibres and the cementitious matrix. The literature information concerning the use of polymer coating on carbon fibre to improve carbon fibre strand integrity and interphase bonding with cementitious matrix is very limited.

In this work, a variation of the ARG fibre diameter and its influence on surface sizings and coatings (part I) as well as the resulting interphase properties (part II) are investigated. The mechanical properties of sized and coated ARG, the surface morphology developed and the fracture energy of the composites achieved will be elucidated as a function of fibre diameter, sizing and coating content as well as their chemical formulations under special consideration of nanotubes and nanoclay. Furthermore, selected nanodispersed polymers will be investigated to improve the tensile strength and the fracture energy of carbon fibre-reinforced concrete.

2. Experimental

2.1. Material

AR-glass fibres (IPF ARG) are made at the Leibniz Institute of Polymer Research Dresden by using a continuous pilot plant spinning equipment [6]. The filament diameter was varied from 13, 17 to 19 μm by the take-up speed of the spin cake winder. The filaments are sized within the continuous spinning by an alkali-resistant sizing consisting of silane coupling agent, γ-aminopropyltriethoxysilane (APS) and N-propyltrimethoxysilane (PTMO), in conjunction with film formers and nanoparticles in the aqueous sizing. The 0.2 wt% multi-wall carbon nanotubes (abbr.: MWNTs,