THERMO-MECHANICAL CHARACTERIZATION OF VGCF- MODIFIED ADHESIVE FOR BOND BETWEEN CFRP AND CONCRETE SUBJECTED TO COMBINED EFFECT OF TEMPERATURE AND HUMIDITY

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ABSTRACT
Adhesives are employed in external strengthening of bond concrete structures by CFRP composite elements. Carbon-based composites are currently the most common type used to increase the strength of concrete members. The application of CF fabric to concrete members involves the use of a compatible bonding agent, and it is the modification of such bonding agents that is investigated in this paper. The investigation involves examining the effects of adding different concentrations of vapour-grown carbon nanofibres (VGCF) (0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%) on the thermal and mechanical properties of the bonding agent. The effect of modification on the glass transition temperature and heat flow of the modified adhesive was explored using DSC technique. It was found that $T_g$ reduces slightly or remains the same with the addition of VGCF to Part A of the adhesive and the highest reduction in $T_g$ was found when Part A was reinforced with 2 wt % VGCF. Agglomeration of the fibres was observed when VGCF was introduced into MBrace® Saturant epoxy adhesive using the speed mixer and a random orientation for the fibres was noted within the epoxy matrix. Peeling-off of CF fabric was the common failure mode as the loaded CFRP/concrete system was subjected to the combined effect of temperature and humidity after short periods of exposure to such severe conditions.

KEYWORDS
VGCF, carbon nanofibers, CFRP, Concrete, modified adhesive, durability.

INTRODUCTION
Carbon fibre-reinforced polymer (CFRP) composites have been widely used for retrofitting and strengthening of concrete structures due to their attractive properties such as strength, stiffness and durability. CFRP composites can be used for different strengthening applications such as in torsion (Hii and Al-Mahaidi 2006), shear (Lee and Al-Mahaidi 2008) and flexure (Pham and Al-Mahaidi 2004 a,b). The application of CFRP to concrete members involves the use of a compatible bonding agent. Thermosetting polymers are widely used as a matrix for CFRP composite materials as well as bonding agents for CFRP composites used in strengthening concrete structures.

Due to their excellent thermal and mechanical properties, carbon fibres are commonly used in polymer matrix composites and are found in various classes depending on the production process. Vapour-grown carbon nanofibre (VGCF) is one of these classes which is used to reinforce polymers and produce nanocomposites. This is due to their unique properties, which include low-cost fabrication (Zeng et al. 2005), high strength and stiffness and excellent thermal conductivity (Tibbetts 1992). The great advantage of VGCFs is that their diameter can be arbitrarily small and limited from below, not by the thickness of the initial polymer fibre, as in pitch- and polyacrylonitrile-based fibres, but by the minimum theoretical diameter of a monomolecular carbon nanotube (0.7 nm). Nanofibers proper are VGCFs less than 0.1 mm in diameter: at such diameters, the properties of a fibre, particularly its strength, change qualitatively. A significant enhancement in the final properties of the composites can be achieved by the addition of...
such nanomaterials to adhesives used in such applications (Patton et al. 1999, Choi et al. 2005). The glass transition temperature ($T_g$), tensile strength and storage modulus of the polymers are all improved when reinforced with VGCF (Park et al. 2007, Zhou et al. 2007).

The work in this paper is continuing the investigation that reported previously by authors (Al-Safy et al. 2011) to address the thermal and mechanical characterization of the effect of modifying an adhesive used in the CFRP/concrete system with VGCF. In the present work, the effect of modification on the glass transition temperature and heat flow of the modified adhesive was explored using DSC technique. The dispersion of VGCF within the epoxy adhesive was demonstrated using TEM. Single-lap shear tests were employed to detect the effect of such modification on the interface bond between CFRP and concrete substrates under harsh environmental conditions.

MATERIALS

A commercially-available bonding adhesive, MBrace® Saturant (BASF, Chemical Construction, Pty. Ltd, Australia) is used for modification in the present work. The adhesive is a two-part system of ambient temperature curing and it is a commonly-used thermosetting polymer for bonding CFRP materials to concrete substrates. The adhesive is a two-part system of ambient temperature curing with a mixing ratio of (100:30) (Part A:Part B) with a glass transition temperature ($T_g$) of 70ºC (DMTA) for ambient temperature curing (Al-Safy et al. 2009).

A commercially-available carbon nanofibre, PR-24 XT-LHT (Pyrograf®-III, Applied Sciences, Inc., USA) is used in this study to modify the bonding adhesive at different concentration levels. VGCF is a black, fluffy agglomerates. The average of fibre diameter is 100 nm as provided by the manufacturer.

The CFRP material used in this investigation is a normal modulus CF fabric commercially available as MBrace CF 130 (S & P C-Sheets 240) supplied by BASF Chemical Construction Pty. Ltd, Australia. CF-fabrics are of 240 GPa fibre modulus and 3800 MPa of tensile strength according to the manufacturer.

Concrete substrates of 75 × 75 × 250 mm dimensions were produced from normal strength concrete mix. The average recorded compressive strength of the concrete was 35 MPa after 28 days of curing.

VGCF-MODIFIED ADHESIVE

A Speed Mixer™ DAC150 FVZ is used to mix VGCF with part A of MBrace® Saturant epoxy adhesive. The required amount of VGCF was added to a pre-calculated amount of Part A of MBrace® Saturant epoxy adhesive in the mixing container of the speed mixer. The mixing container with a lid was placed in the mixing cup basket of the speed mixer. The mixing procedure was carried out for 15 minutes at 2000 rpm. The hardener, Part B, was then added to the mixture (Part A and VGCF) and mixed manually for a few minutes in order to get a homogeneous mixture.

FABRICATION OF CFRP/CONCRETE SPECIMENS

The surface of the concrete substrates was prepared for bonding by using sandblasting method in order to remove dirt and latent material to expose the coarse aggregates from the area for strengthening with CFRP. A thin layer of primer was applied on the cleaned area of the concrete. Samples were left for 1 h at ambient temperature for curing. A wet lay-up method was used for CFRP application. In this method, VGCF-modified adhesive was used as bonding agent and to saturate CF fabric and placed on the bonded area using a roller. CFRP/concrete samples were then left at ambient conditions for more than 7 days.
TESTING PROCEDURE

Differential Scanning Calorimetry (DSC)

DSC was used to thermally scan solid samples of ambient temperature curing from 20ºC to 120ºC at 10ºC/min heat scanning rate. The samples were then held isothermally for 1 min at 120ºC and then cooled from 200ºC to 20ºC at the same scanning rate and held for 1 min at 20ºC. The final heating cycle was then undertaken at 10ºC/min, as for the first cycle.

Transmission Electron Microscopy (TEM)

The dispersion of nanomaterials into the MBrace® Saturant epoxy adhesive was explored using Transmission Electron Microscopy (TEM). Adhesive specimens for TEM examination were prepared by ultra-microtoming at ambient temperature. Small triangular sections (with a base of 5 mm in length) were mechanically cut from a larger size of bulk material. A nominal thickness of 80 nm was achieved from the small triangular sections using a diamond knife. Sections were subsequently sandwiched between two 400-mesh copper thin bar grids and the grids were then separated, with the specimen retained on one of the grids. Bright field TEM images were obtained at an accelerating voltage of 200 kV with a Phillips CM20 electron microscope in which an electron gun emits an electrical beam.

Accelerated Durability Tests for CFRP/Concrete System

Four loaded CFRP/concrete samples using VGCF modified MBrace® Saturant epoxy adhesive as an adhesive were subjected to an accelerated test (A1) based on constant temperature (50ºC) and ramped humidity from 30% to 90% for 21 days (504 h). Another four loaded CFRP/concrete samples were subjected to an accelerated durability test (A2) based on constant humidity (90%) and cyclic temperature (20-50ºC) for 44 days. Steel frames (1×1×1 m^3) were used to place and hold the CFRP/concrete specimens. These frames were placed inside an environmental chamber and were used to provide a permanent sustained load inside the exposure system during the test period. The frames were capable of sustaining applied loads without significant loss by using springs of 4 mm displacement for each 1 kN loading.

RESULTS AND DISCUSSION

DSC Measurements

A summary of the first and second heating scans from DSC traces is shown in Figure 1 (left and right) respectively for VGCF-modified adhesives. The DSC traces for the control mix (0 %VGCF) in Figure 1 were obtained from our previous reported work (Al-Safy et al. 2012). In relation to the first heating scan, the shape of the shift in the heat flow for unmodified cross-linked epoxy system (MBrace® Saturant) (0% VGCF) and modified adhesives with different concentration of VGCF (0.5,1,1.5 and 2wt%) was found to be the same, whilst for the second heating scan the heat flow curves of all modified adhesives stepped slightly up-word than the control. T_g reduces slightly or remains the same with the addition of VGCF to Part A. The highest reduction in T_g was found when Part A was reinforced with 2 wt % VGCF. A difference in T_g from the two heating scans was found, as higher values were yielded by the second heating scan. The ultimate T_g was found to be higher by 1-3°C from T_g from the first scanning heat for the control epoxy adhesive (without modification) and for the epoxy adhesive reinforced with 0.5 %, 1 and 2% of VGCF (Table 1). However, a greater variation in T_g was detected for epoxy adhesive with 1.5wt% VGCF from the values for the two heating scans for the same sample.
Figure 1: DSC thermograms for MBrace® Saturant epoxy adhesive modified with different VGCF concentrations: first heating scan (left), and second heating scan (right)

Table 1: DSC measurements of MBrace® Saturant adhesive modified with various percentages of VGCF

<table>
<thead>
<tr>
<th>VGCF (wt %)</th>
<th>Onset $T_g$ (°C)</th>
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TEM Micrographs

The dispersion of commercially-available carbon nanofibres in vapour-grown phase PR-24 XT-LHT using the speed mixer was characterized using different TEM magnifications. Figure 2 show the structure of the epoxy matrix reinforced with different concentrations (0.5, 1, 1.5 and 2 wt%) of VGCF using speed mixing. For all VGCF percentages, random dispersion of the nanofibres was detected from TEM thermograms. The orientation of the fibres is not in the same direction for all fibres within the same mix. Within the epoxy matrix, the nanofibres were observed in transverse cross-sections, in addition to their axial sections with different shapes of fibre (indicated as arrow A in Figure 2 (c)). The length of nanofibres varies between long fibres and short fibres.

TEM images also show agglomeration of the fibres within the epoxy matrix due to their high aspect ratio, high surface and numerous van der Waals interactions. This is shown clearly under medium magnification in Figure 2 (a) for an epoxy matrix reinforced with a low concentration (0.5wt%) of VGCF, and under low magnification for an epoxy system reinforced with 2wt% in Figure 2 (d). Such agglomerated bundles act as barriers to the transfer of force from the matrix to the nanofibres. Debonding between the epoxy matrix and PR-24 XT-LHT within the nanoadhesive is characterized by the availability of bright areas in all TEM images, which reflect the adhesion level between the epoxy matrix and VGCF. These areas are identified by black arrows in Figure 2.

![Figure 2: TEM images for MBrace® Saturant epoxy adhesive modified with: (a) 0.5%wt VGCF, (b) 1 wt% VGCF, (c) 1.5 wt% VGCF, and (d) 2 wt% VGCF](image-url)
Concrete substrates externally strengthened with CF fabric were subjected to two different series of accelerated durability tests in order to investigate the bond endurance of CFRP/concrete samples using VGCF-modified adhesive. Two ratios of VGCF were chosen to reinforce Part A of MBrace® Saturant: a low percentage of VGCF (1 wt%) and a high percentage of VGCF (2 wt%), which is the highest percentage of VGCF found to saturate the adhesive after many trial mixes. In total, four CFRP/concrete specimens were exposed to an accelerated durability test (A1), based on constant temperature (50°C) and ramped humidity in the range of 30-90 % for 21 days (504 hrs). All CFRP/concrete samples failed in the environmental chamber after only 24 hrs from the start of the exposure program. The failure was found in the interface between the primer and the adhesive for samples of 1 wt% VGCF as shown in Figure 3(left). However, a combination of failure in primer/adhesive interface and primer/concrete interface was found for samples with 2 wt% VGCF-modified adhesive, as shown in Figure 3(right).

Figure 3: CFRP/concrete samples failed inside the environmental chamber for A1 accelerated test using modified Part A of MBrace® Saturant with : 1 wt%VGCF (left) and 2 wt% VGCF (right)

Figure 4 illustrates the failure pattern of four CFRP/concrete samples, using two different concentrations of VGCF reinforcement (1 wt% and 2 wt%), which failed in the environmental chamber when subjected to another accelerated durability test (A2) based on constant humidity (90%) and cyclic temperature (20-50°C) under sustained load of 40% of the ultimate load. The CFRP/concrete system failed in the environmental chamber after only 48 hrs of exposure to harsh service conditions. The failure mode in Figure 4 for 1 wt% and 2 wt% of VGCF is characterized as a combined failure mode: failure in the primer/concrete interface and some areas show failure in the primer/adhesive interface, as illustrated in the close-ups for the failure patterns in Figure 4.
Figure 4: CFRP/concrete samples failed inside the environmental chamber for A2 accelerated test using modified Part A of MBrace® Saturant with: 1 wt% VGCF (left) and 2 wt% VGCF (right)

CONCLUSIONS

The effect of introducing VGCF as an additive to the adhesive used in CFRP/concrete system was investigated. The structure of the modified adhesive and bond performance of CFRP/concrete at different severe operating conditions were investigated. The following observations can be made and conclusions drawn:

1- Adding different percentages of a commercially-available VGCF (PR-24 XT-LHT) (up to 2 wt%) to a commercially-available epoxy adhesive using the speed mixer reduces $T_g$ slightly or remains the same. The highest reduction in $T_g$ was found when Part A was reinforced with 2 wt% VGCF. The minor influence of the additive on $T_g$ in this investigation is believed to be due to the slight effect of the additive on the cross-linked epoxy network.

2- TEM characterization of VGCF-modified adhesive showed that the introduction of VGCF into a commercially-available epoxy adhesive such as MBrace® Saturant using a speed mixer produces agglomerates of the fibres randomly oriented within the epoxy matrix.

3- The endurance of CFRP/concrete systems using VGCF-modified adhesive is affected by exposure to harsh service conditions. Peeling off of CF-fabric was the most common failure mode when the loaded CFRP/concrete system was subjected to the combined effects of temperature and humidity after short periods of exposure to such severe conditions. The primer/adhesive interface is influenced due to the low adhesion strength between the primer and the adhesive which allows the moisture to penetrate the primer/adhesive interface and causes bond loss within a few days of exposure to the combined effects of temperature and humidity.
REFERENCES


