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Thermal and oxidation resistant barrier on carbon fiber with Si and Si–Ti based pre-ceramic coatings for high temperature application

Mohammad Abu Shayed, Heike Hund, Rolf-Dieter Hund and Chokri Cherif

Abstract

Carbon fiber (CF) must be protected from thermal oxidation for high temperature application because of its low thermo-oxidative stability above $450°C$ in air. CF is now increasingly being used as a reinforcing material in the construction industry. A thermal and oxidation resistant coating is necessary for CF-reinforced concrete (CFRC) composites in order to satisfy a high level of safety standard in the case of fire. New types of pre-ceramic coatings, such as Tyranno® polymer (Si–Ti based pre-ceramic) and SiO_2 sol–gel, have been deposited on CF filament yarn by means of a wet chemical continuous dip coating method. The results of surface analyses, e.g. scanning electron microscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy, showed the changes in topographical properties of CF caused by the coatings. Thermogravimetric analysis proved that the high temperature (up to $800°C$) oxidation stability of CF was considerably improved due to the coatings. Tensile test results indicated that the strength of CF yarn at $20°C$ was increased by up to 80% with the coatings. Thermo-mechanical properties were also enhanced up to $600°C$. CF yarn retains its original strength and elasticity modulus, i.e. the stiffness at $700°C$, with a Tyranno® polymer coating.

High performance materials from carbon fiber (CF) possess great importance for the development of composites in high tech applications due to their light weight, very high strength, and stiffness properties. For example, CF-reinforced concrete (CFRC) composites in architecture and civil engineering are a new promising application area, where steel in reinforced concrete can be replaced by CF. The major limitation of construction steel is its inferior thermo-mechanical properties at high temperature. This steel material loses its mechanical properties rapidly from $300°C$ and the loss of strength and stiffness are found to be more than 90% up to $750°C$.[1] For this reason, CFRC composites are very promising for increased usage in the fabrication of new building components as well as in repairing and strengthening of existing structural components due to their lightweight, superior mechanical, and

thermal properties compared to steel in reinforced concrete. These composite materials must be sustained under thermo-mechanical loading because of the high level of safety and security demands in the case of fire. They must also fulfil the fire resistance standards of building components.[2] In addition, CF and its composites, such as carbon/carbon (C/C) composites and CF-reinforced ceramic matrix composites, are

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increasingly used for high temperature applications, e.g. in the space, general engineering, automotive, and energy sectors.[3–4]

In spite of the excellent physico-chemical properties and very good thermal stability of CF in an oxygen-free environment at high temperature, it also has limitations. Low thermal stability at elevated temperatures in the presence of oxygen, which is a major problem of CF, results in the reduction of thermo-mechanical properties.[5] CF remains intact up to a temperature of 450°C in atmospheric air.[6] Thus, CF can be used in high temperature (from 500°C) applications under atmospheric conditions, provided thermal oxidation is prevented. In addition, the surface of CF is highly inert, which affects chemical interactions at the fiber–matrix interfaces and thus negatively influences the mechanical properties of the composite. So, the modification of fiber surface is also important to improve the adhesion between fiber and matrix. CFs are normally treated with sizing materials at the last stage of their manufacture to protect the fiber from damage during further processing, as well as to ensure a proper bonding between the fiber and matrix materials. Epoxy and polyurethane-based sizing, which are principally used for CF, are suitable for the processing of fiber in either a thermoplastic or thermoset matrix.[7] However, these sizing materials cannot protect CF from high temperature oxidation. So, there is a demand for a thermal and oxidation protective coating for the high temperature application of CF.

Numerous research works have been reported on CF oxidation and the development of various coating systems for the protection of CF from thermal oxidation. [8–14] Most of these coatings are based on ceramics such as refractory oxides, carbides, borides, or nitrides. Although these ceramics have good thermal and mechanical properties, they have low toughness, which leads to crack formation under thermo-mechanical stresses at high temperatures.[15] Furthermore, high temperature resistant coating of CF is a most challenging issue because of its chemical inertness, very smooth surface, and negative thermal expansion coefficient. Hence, it is necessary to develop an ideal coating system which can fulfil the requirements of a heat and oxidation barrier coating, such as very low thermal expansion coefficient similar to CF, high temperature stability, oxidation resistance, cracks deflection ability, and chemical compatibility with fiber and matrix. Mostly, an oxidation resistant coating is deposited onto CF by physical vapor deposition (PVD) or chemical vapor deposition (CVD) processes. However, these processes are discontinuous and very costly. A homogeneous coating of all individual filaments in the filament bundle is not possible with these processes. For the customized application of heat resistant coatings from an aqueous medium, a wet chemical continuous dip coating method offers high potential over the aforementioned established methods of coating. The advantages of a wet chemical dip coating process over PVD and CVD coating processes are higher productivity, less energy consumption during processing, homogeneity of coating on all individual filaments in the CF filament bundle, and environmental friendliness. However, intensive investigations need to be performed to optimize the processing parameters in the wet chemical dip coating process for the application of different thermal and oxidation resistant coatings on CF filament yarns.

In order to deposit a homogenous coating layer on each individual CF filament of a bundle, it is necessary to choose an appropriate coating material and a suitable coating process. Liquid-phase coatings based on organic–inorganic hybrid polymers known as pre-ceramic precursors are currently being used as thermal and oxidation protective systems for carbon/carbon (C/C) composites, metals, and ceramic matrix composites.[16–20] At high temperature (above 500°C), pre-ceramic polymers become crosslinked by thermal, chemical, or photochemical treatment and are converted into the ceramic layers.[20,21] Moreover, Tyranno® polymer is a novel two-component coating system. In addition, sol–gel coatings have gained research importance for deposition of a ceramic layer onto CF.[22] The main target of our study was to develop new coating systems for the thermal and oxidation protection of reinforcing CF yarn for CFRC. In order to fulfil the objectives of the research, thermal and oxidation resistant pre-ceramic coatings such as Tyranno® polymer (Si–Ti based pre-ceramic) and SiO_2 sol–gel (Si based pre-ceramic) had to be deposited onto CF yarn by means of a wet chemical continuous dip coating method. After the coating, the coated samples were characterized to evaluate the coating performance. It should be mentioned that the investigation of Tyranno® polymer on CF by a continuous dip coating process for fire resistant CFRC is presented in this research for the first time. This Tyranno® polymer is converted to Si–Ti ceramics at high temperature (above 500°C), which can restrict the thermal oxidation of CF effectively. In addition, a SiO_2 sol–gel coating has been applied to CF yarns for CFRC structures to fulfil the high standard of fire resistance. This has also not been investigated previously for CFRC.

Experimental details

Materials and methods

Toho Tenax carbon filament yarn (Tenax®-E HTS40 F13) with a fineness of 800 tex (number of filaments: 12,000, filament diameter: 7 μm) supplied by the

producer Toho Tenax Europe GmbH, Wuppertal, Germany, was used as the substrate for coating in this study. These CF yarns, pre-treated with polyurethane based sizing, were used as received.

The coating experiments were carried out using two different liquid phase pre-ceramic precursors, namely Tyranno® polymer and SiO_2 sol. Tyranno® coat Varnish VN-100 (44–49% solid content) type polymer purchased from Ube Industries Ltd, Tokyo, Japan, is an inorganic–organic hybrid polymer produced from the mixture of polyalkylphenylsiloxane and poly(carbosilane-siloxane)-titanoxane. Figure 1(a) shows the formation of poly(carbosilane-siloxane)-titanoxane-siloxane. Firstly, poly(carbosilane-siloxane)-titanoxane is obtained through the condensation of poly(carbosilane-siloxane) and titanium alkoxide. Afterwards, this poly(carbosilane-siloxane)-titanoxane is crosslinked with the polyalkylphenylsiloxane to get Tyranno® coating. Finally, silicon and titanium ceramic structures can be formed by the pyrolysis of this polymer above 500°C.

The SiO_2 sol was prepared from triethoxyphenylsilane (TEPhSi) precursor (purity 97.5%). The composition of the sol (in molar ratio) was TEPhSi:ethanol (purity 99.8%):water:acetic acid (99–100%) = 1:10:3:2. The formation of a three-dimensional (3D) silicone network structure from TEPhSi sol–gel is illustrated in Figure 1(b). In the first step, the silanol (Si–OH) group containing structure is obtained after the hydrolysis of TEPhSi in the presence of acetic acid as a catalyst. Siloxane (–Si–O–Si–) is formed in the second step due to the condensation reaction of two silanol groups. Finally, the siloxanes are crosslinked with each other to build a 3D silicone network.

After the preparation of the coating solutions, CF yarn was then continuously coated by means of a dip coating method. The experiments were carried out using a Basecoater BC32 (Coatema Coating Machinery GmbH, Dormagen, Germany) laboratory coating machine. The formulations used for coatings are shown in Table 1. The samples C1 and C2 were coated with Tyranno® polymer and SiO_2 sol–gel, respectively. A description of the coating process, parameters, and the method of the calculation of coating percentage on the samples can be found in our earlier study.[21]
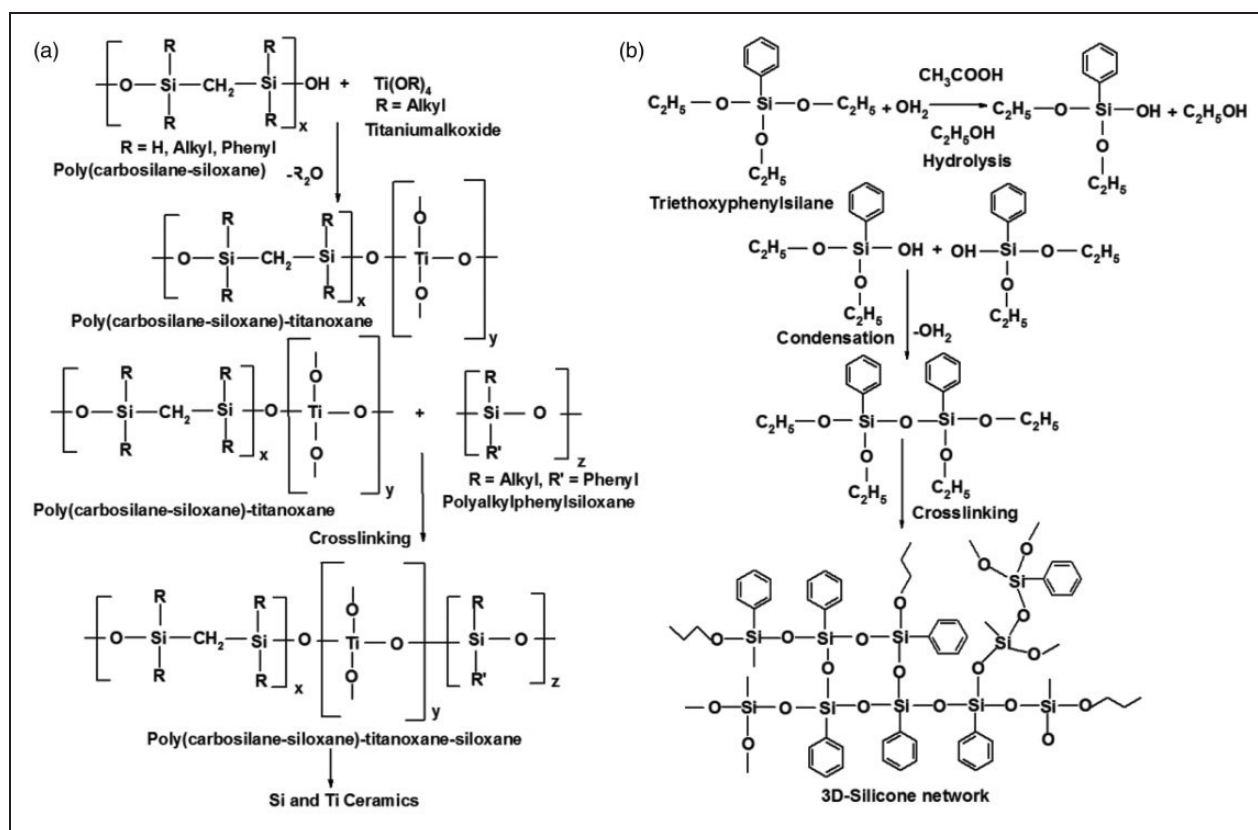

Figure 1. (a) Formation of poly(carbosilane-siloxane)-titanoxane-siloxane and (b) 3D silicone network structure from TEPhSi sol–gel.[23]

Table 1. Coating formulations and process parameters

Sample	Polymer type	Polymer wt %	Ethyl acetate wt %	Curing temperature (°C) and time (min)	Coating % on CF
C1	Tyranno® coat VN-100	25	75	200, 2	9.90 ± 0.30
C2	TEPhSi sol–gel	TEPhSi:ethanol = 1:10 (molar ratio)		140, 2	9.20 ± 0.60

Characterization techniques

The surface morphologies and the microstructures of the samples were investigated by scanning electron microscopy (SEM), type Zeiss DSM Gemini 982, Jena, Germany. X-ray photoelectron spectroscopy (XPS) was conducted to analyze the quantitative chemical compositions as well as chemical nature of sample surfaces. XPS spectra were detected by an ESCA 5700 (Physical Electronics GmbH, Munich, Germany) photoelectron spectrometer with a monochromatic Al K_α X-ray source with corresponding photon energies 1486.6 eV. Fourier transform infrared (FTIR) analysis was carried out using the infrared spectroscope FTIR Nicolet 6700 (Thermo Scientific, Dreieich, Germany) to recognize chemical functional groups on the surface of coated and uncoated CF yarns. The attenuated total reflectance (ATR) FTIR technique and a diamond crystal were used for this purpose. The measurements were performed using a spectrometer configuration capable of detecting in the range from 4000 cm^{-1} to 650 cm^{-1}.

Thermogravimetric analysis (TGA) was carried out to characterize thermal properties such as thermal decomposition and thermo-oxidative stability using the instrument Q500 (TA Instruments, Eschborn, Germany). The samples were heated from 30°C to 1000°C with a 20°C/min heating rate and 50 mL/min flow rate of air. Isothermal TGA at 500°C, 600°C, and 700°C was also performed in an air atmosphere. For activation energy analysis, the sample was monitored with heating rates of 5°C/min, 10°C/min, and 20°C/min.

From the temperature dependence of TGA data, an "activation energy" for the conversion of the untreated CF and coated CF starting material into modified materials (more or less degraded materials) can be obtained.[25–27] Because this conversion is mostly carried out under atmospheric oxygen (air), the corresponding activation energy is often assigned to an oxidation process. However, this conversion is a complex process because it is composed of many components and the solid state structure of the materials (fiber and coating), and therefore the microenvironment for the chemical reactions, will change. This will again influence the chemical reactions. Due to the diffusion of oxygen into the fiber and the diffusion of low molecular weight degradation products out of the fiber, the concentration of reactants and products will change during the oxidation process. Because TGA cannot reflect all these influential factors specifically, an activation energy determined by TGA has a complex meaning. Bearing this in mind, for any statements made in this study in connection with activation energy, the term activation energy is used in this broader sense. The explanation given here is also true for an iso-conversional energy technique, which calculates the effective activation energy (E_a) as a function of the conversion (α) of a chemical reaction, $E = f(\alpha)$. It is based on the Flynn–Wall–Ozawa method.[25,26] The Vyazovkin and Flynn–Wall–Ozawa equations are considered as dynamic equations, which are used for the determination of the activation energy for all conversion values (α). Logarithm of heating rate ($\ln \beta$) versus reciprocal temperature can be plotted from the TGA data with different heating rate by MS® Excel software, which gives a straight line with slope m. The activation energy is then estimated from the slope ($m = -E_a/R$) for each conversion.

The mechanical and thermo-mechanical properties of CF yarn were examined using a Zwick tensile testing machine Z 100 (Zwick GmbH & Co. KG, Ulm, Germany). The test was performed according to the standard test method ISO 3341 at (20 ± 2)°C temperature and (65 ± 2)% relative humidity. The actual set up of the tensile testing and the measurement procedure can be found in our previous publication.[24] The test was carried out at room temperature (20 ± 2)°C and under thermal stress at 300°C, 400°C, 500°C, 600°C, 700°C, and 750°C respectively. The sample was heated inside the tube furnace with an IR heater at 20°C/min and the temperature was monitored by a sensor.

Results and discussion

Surface morphological analysis

SEM analysis. Figure 2 shows the SEM images of uncoated and coated samples. The SEM microphotograph of uncoated CF shows a relatively smooth and homogeneous surface. The capillary effect is clearly identified in uncoated CF filament surface, which extends to the whole length of the filament (Figure 2(a)).
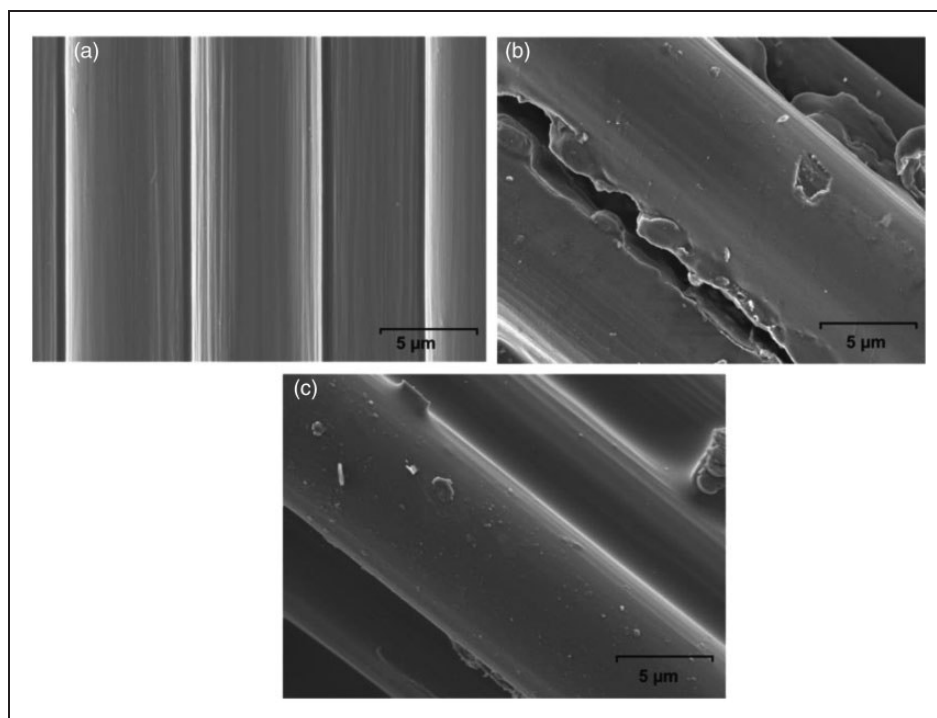
Figure 2. SEM images of (a) uncoated and coated CF yarns with (b) C1 and (c) C2 coatings.

It can be seen from the SEM images that considerable changes of surface topographical properties are revealed in Tyranno® polymer (C1) and SiO_2 sol–gel (C2) coated CF yarns. The sample C1 exhibits a smooth and relatively homogenous coating layer with cracks between the individual filaments and void on the surface, which may be caused by defective coatings (Figure 2(b)). However, the individual CF filaments are bridged together due to Tyranno® and SiO_2 sol–gel coatings. The bonding of filaments to each other may be explained due to the crosslinking of pre-ceramic polymers. As a result, the mechanical properties of CF yarns are improved after coating. However, the crack between the filaments has no considerable effects on the mechanical properties of coated CF (cf. the section of mechanical and thermo-mechanical properties). It can be concluded from the SEM results that the surface topographical properties of CF were improved due to the pre-ceramic coatings. These coatings could be used to modify interphase properties by minimizing the surface defects of CF and hence the durability in extreme conditions (high temperature and high alkaline environment) might be improved by such barrier coatings.

XPS analysis. Table 2 summarizes the atomic percentages of uncoated and coated CF samples obtained from XPS analysis. XPS survey spectra of the samples are reproduced in Figure 3. The XPS spectrum of the uncoated CF shows the presence of three distinct peaks due to carbon, nitrogen and oxygen. In contrast,

Table 2. XPS results of uncoated and coated CF

Sample	Atom percentage (%)			
	C 1s	O 1s	N 1s	Si 2p
Uncoated CF	72.7	25.2	2.1	–
C1	63.0	20.9	–	16.1
C2	64.0	24.3	–	11.7

characteristic silicon peak along with carbon and oxygen can be observed in both of the coated samples. However, nitrogen is not detected on surface of coated samples. It can be stated that the XPS detects up to few nanometers depth, therefore nitrogen was not detected in the case of coated CFs. It can be clearly seen in Table 2 that the chemical composition of CF surface is changed due to heat and oxidation resistant pre-ceramic coatings. The oxygen and carbon found at the surface of uncoated CF are due to the sizing material, which is applied at the last stage of CF manufacture. Remarkably, the Tyranno® polymer coated sample C1 shows higher silicon concentration than the sample C2.

Additionally, the different photopeaks, such as C 1s, O 1s, N 1s and Si 2p (Figure 3), detected at the specific ranges of binding energies demonstrate the existence of various functional groups in the samples depending on the type of coating used. The C 1s peak may be due to
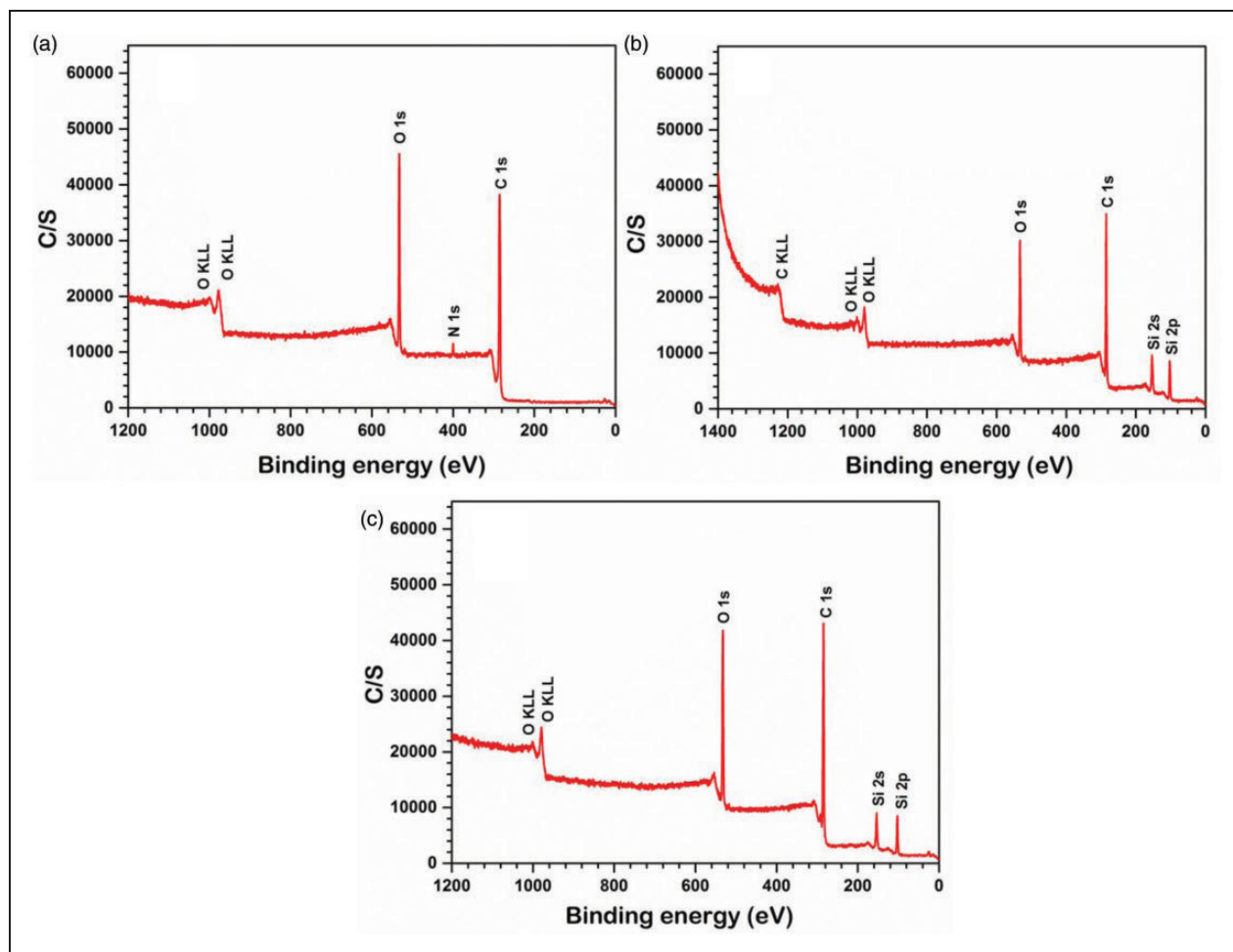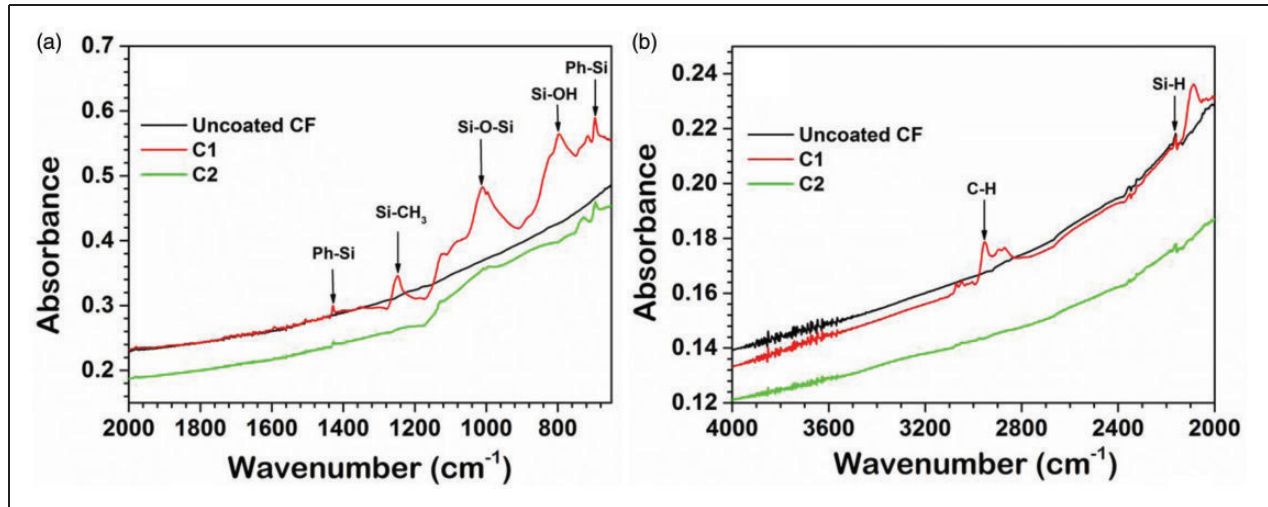
Figure 3. XPS spectra of (a) uncoated CF and coated samples (b) C1 and (c) C2.

the presence of aromatic carbon and O 1s peak is responsible for ketone or carboxylic groups at the surface of uncoated CF (sized CF). The availability of N 1s peak in uncoated CF is attributed to the nitrile or urethane group. In contrast, the C 1s peak of coated samples (C1 and C2) may be recognized as due to the aliphatic or aromatic carbon depending on type of coating. Besides, the existence of O 1s peak can be explained in terms of the alcoholic or carboxylic groups in coated samples. The recognition of Si 2p peak in the coated samples C1 and C2 is assigned to the silicon oxide as well as organosilicon containing functional groups such as silanol, methyl-, or phenylsilicon.

From the XPS results, it can be found that the Tyranno® polymer (C1) coated sample contains higher amount of silicon at its surface compared to that of the SiO_2 sol–gel (C2) coated sample. Consequently, the higher ceramic yield could be obtained from the Tyranno® polymer coating.

FTIR analysis. Figure 4(a) and (b) illustrate the FTIR spectra of uncoated and coated CF in the spectral ranges $650–2000 \, cm^{-1}$ and $2000–4000 \, cm^{-1}$, respectively. No characteristic peaks are detected in uncoated CF in the spectral range from 650 to $2000 \, cm^{-1}$ (Figure 4(a)). A small peak at $2150 \, cm^{-1}$ may indicate the existence of an aromatic band in uncoated CF (Figure 4(b)). During IR analysis, not much structural information is found in uncoated CF due mainly to the difficulty to record a good quality spectrum with conventional techniques owing to the highly absorbing nature of the uncoated CF sample.[28]

However, there are some characteristic absorption peaks found in the coated samples due to the modification of CF yarn by thermal and oxidation resistant coatings (Figure 4(a) and (b)). The peak of Si–O–Si at $1000–1100 \, cm^{-1}$ is clearly visible in coated sample C1. There are some other absorption peaks apparent in the FTIR spectrum of this sample, e.g. peaks of Si–CH$_3$ at $1260 \, cm^{-1}$, Si–H at $2160 \, cm^{-1}$, and C–H at $2971 \, cm^{-1}$.

Figure 4. FTIR spectra of uncoated and coated CF yarns in the spectral ranges (a) from 650 to 2000 cm^{-1} and (b) from 2000 to 4000 cm^{-1}.
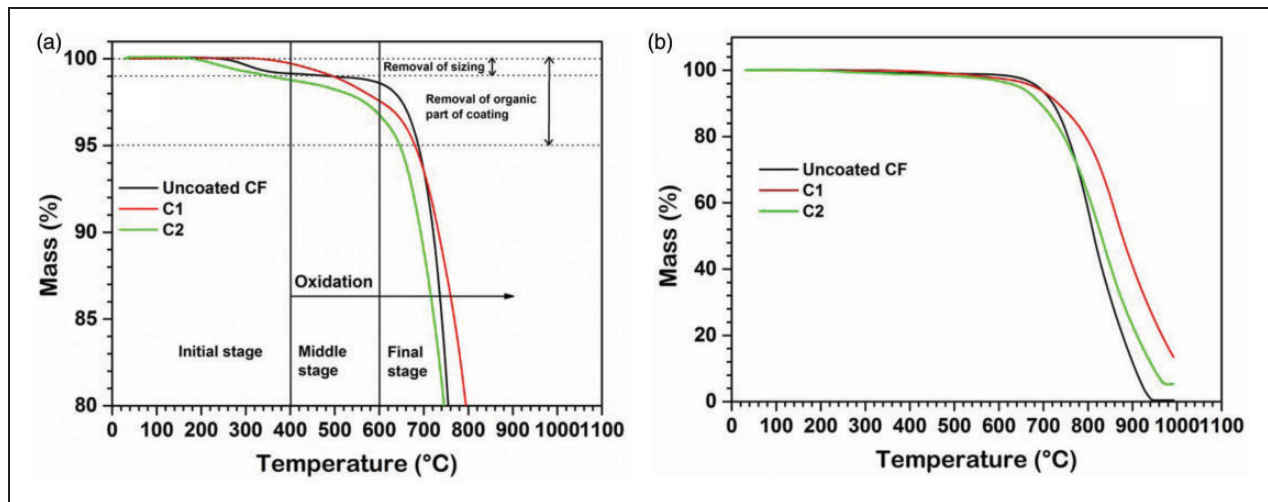
Figure 5. TGA curves of uncoated and coated samples with (a) 20% and (b) 100% mass loss in an air atmosphere.

On the other hand, small peaks of Si–O–Si at 1000–1100 cm^{-1}, Si–OH at 800 cm^{-1}, and Si–H at 2160 cm^{-1} are visible in the SiO$_2$ sol–gel coated sample C2. These peaks are characteristic for silane, organosilicon, or fully organic structure. The typical peaks at 690–700 cm^{-1} and at 1430 cm^{-1} are observed in the case of both the coated samples C1 and C2 owing to the presence of the Ph–Si group.

The results of FTIR analysis clearly reveal that the surface interaction between the fiber and polymer coating can be enhanced. Some functional groups are recognized on the surface of coated samples. These will be favorable for the strong adhesion between the CF surface and the matrix in final composite materials.

Thermogravimetric analysis (TGA)

TGA under air atmosphere. TGA curves under ambient air are illustrated in Figure 5. The mass change of the samples can be referred to three temperature stages specifically: initial (30–400°C), middle (400–600°C), and final stage (600–900°C). Figure 5 shows that the mass change rate is very low in the initial stage (30–400°C) for the uncoated and coated CF. In this stage, a mass loss of 0.85% of uncoated CF (as received) occurs due to the removal of sizing material from the uncoated CF sample. On the other hand, coated CF samples lose their mass more slightly (0.27% for C1 and 1.22% for C2) at this stage due to

the evaporation of solvent and moisture from the samples. In the middle stage (400–600°C), a slow oxidation occurs both in the case of uncoated and coated CF. In this stage, the uncoated CF is oxidized slowly and 1.40% mass loss is found up to 600°C. The coated samples C1 and C2 lose, respectively, 2.40% and 3.20% mass up to 600°C due to the volatilization of oligomer of the coating material and the oxidation of organic groups (methyl, ethyl, phenyl, propyl, and vinyl), which are attached to the silicon. It is to be noted that the decreasing order of thermal stability of these groups is phenyl > methyl > ethyl > propyl > vinyl.[29]

The final stage (600–900°C) of TGA is referred to as the rapid decomposition phase. In this stage, rapid oxidation occurs and the coated and uncoated CF samples lose their mass very rapidly. At 700°C, the uncoated CF and Tyranno® polymer coated sample C1 lose nearly 6.5% mass, with the mass loss of sample C2 found to be highest 11.1%. The higher mass loss of the sample C2 between 600°C and 700°C may occur due to the random scission of polymer chains. The structure and composition of the polymer residue change as the thermal degradation advances for that sample, resulting in pure SiO_2 above 600°C.[30] The mass loss amounts to 90% for uncoated CF yarn at 900°C, whereas the coated samples C1 and C2 lose, respectively, 60% and 77% of their mass. The major mass loss from 700°C to 900°C occurs in the uncoated CF sample because of very rapid oxidation. On the other hand, the mass reduction rate is somewhat slower for the coated sample C1 compared with the uncoated CF in this temperature range. In this stage, Tyranno® polymer and sol–gel precursor are converted into ceramic layers, which slow down the oxidation rate of CF. In addition, a reduction in the porosity of the coatings may result from the formation of silicon dioxide, which leads to a lower diffusion rate of oxygen through the pores.[5] But, the mass loss, i.e. the oxidation of CF, cannot be entirely stopped by coatings due to the porosity of the coating layer as well as some micro cracks that may develop during the heating at high temperature. Cracks are caused by the difference in the thermal expansion coefficients of the CF and the coating material.

Isothermal TGA analysis. Isothermal TGA at 500°C, 600°C, and 700°C was carried out to investigate the long-term oxidation behavior of CF. Here, the samples were firstly heated from 30°C to desired temperatures (500°C, 600°C, and 700°C) at a 20°C/min heating rate with an inert N_2 gas flow. Afterwards, the sample was isothermally heated with an ambient air flow. The mass loss versus time was recorded during TGA measurement. Figure 6 shows isothermal TGA curves at 500°C, 600°C, and 700°C. The mass loss increases linearly with time and the slope of the isothermal oxidation curves rises with the increase of temperature both for the uncoated and coated samples. After oxidation in air at 500°C for 305 min, the mass loss of the uncoated CF is found to 14.5%, but the sample C1 loses nearly 12% mass during this time. Initial mass loss (while the temperature raises from 30°C to 500°C, 600°C, and 700°C in N_2 atmosphere) occurs due to the removal of sizing material from uncoated CF and to the evaporation of moisture and volatile oligomers from the coated samples. Then the mass loss proceeds because of the oxidation of both the uncoated and coated samples.

It is obvious from Figure 6 that the coated samples are oxidized at a lower rate during isothermal heating at 600°C compared to that of uncoated CF. A possible reason for the lower oxidation rate of coated samples at that temperature is the formation of ceramic layers on the surface of CF, which act as a heat and oxidation barrier. The coated sample C1 loses 50% of its mass within 180 min owing to isothermal oxidation in static air at 600°C, whereas the same 50% mass decrease is observed in case of uncoated CF after 95 min. At 700°C, the same tendency of the results was observed as for isothermal TGA at 600°C both for uncoated and coated samples. From these isothermal TGA results, it can be concluded that the heat and oxidation resistant pre-ceramic coatings protect CF from oxidation, but these coatings could not entirely stop the oxygen ingress. Tyranno® polymer (C1) coated samples shows better oxidation resistant properties compared to SiO_2 sol–gel coated sample C2 under isothermal conditions.

Activation energy analysis. An activation energy for the change of uncoated and coated CF when heated in air is obtained from the dependence of mass loss data on the heating rate. It is estimated according to the Flynn–Wall–Ozawa method described in the previous section. Figure 7(a) illustrates the TGA traces of Tyranno® polymer coated sample C1 when it was heated with rates of heating 5°C/min, 10°C/min, and 20°C/min. From these TGA data, ln (logarithm) of heating rate versus reciprocal temperatures is plotted for each conversion, which gives a straight line with the slope m (Figure 7(b)). Therefore, the activation energy (E_a) for each conversion is calculated from the slope of the line ($m = -E_a/R$). The temperature ranges from 400°C to 880°C are chosen for the calculation of activation energy up to 50% conversion. Similarly, activation energies up to 50% conversion are determined for uncoated CF and coated sample C2.

The influence of coatings on the thermo-oxidative stability of CF, as reflected by an activation energy obtained by TGA, is shown in Figure 8. It is evident
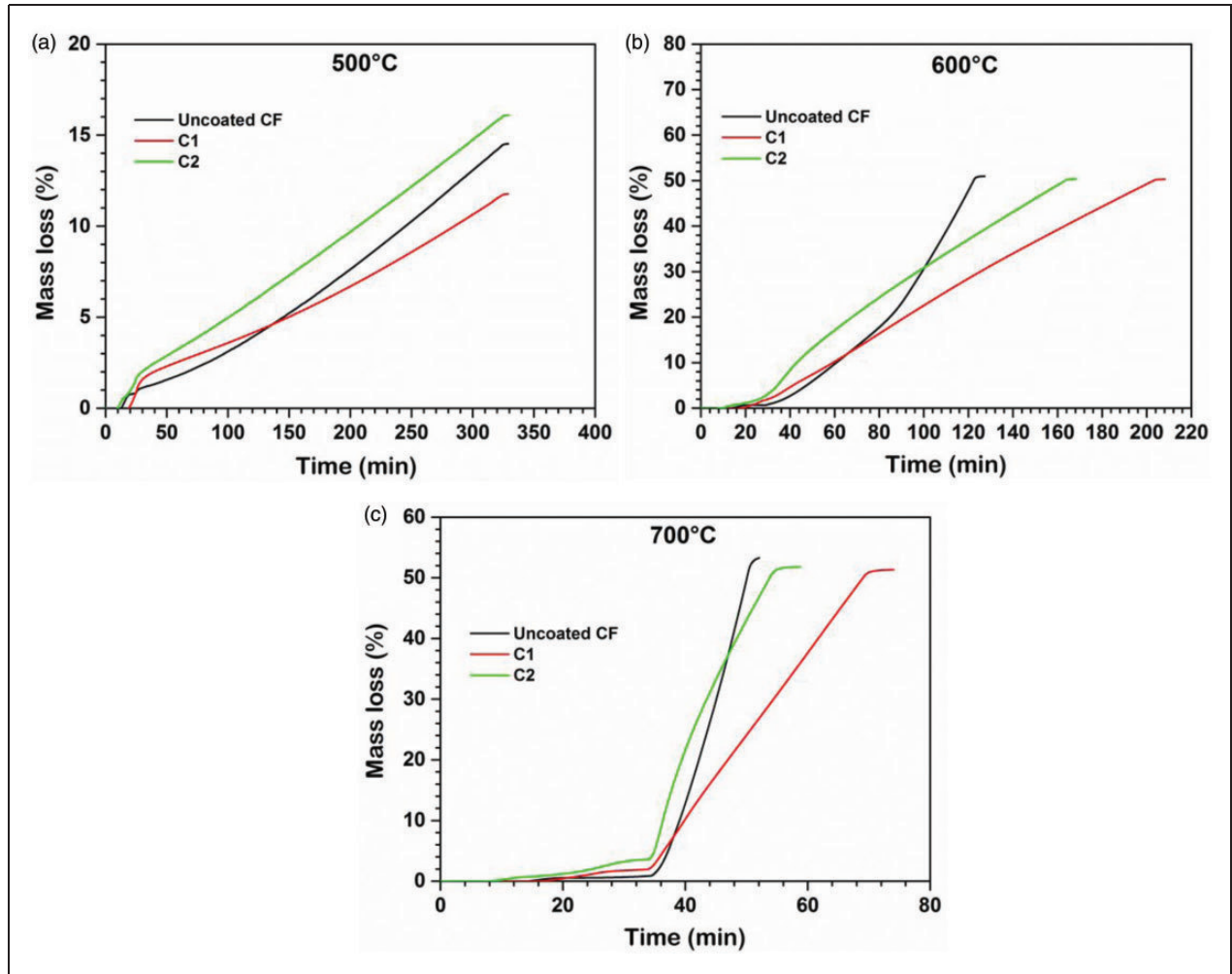
Figure 6. Isothermal TGA curves of uncoated and coated samples at 500°C, 600°C, and 700°C.
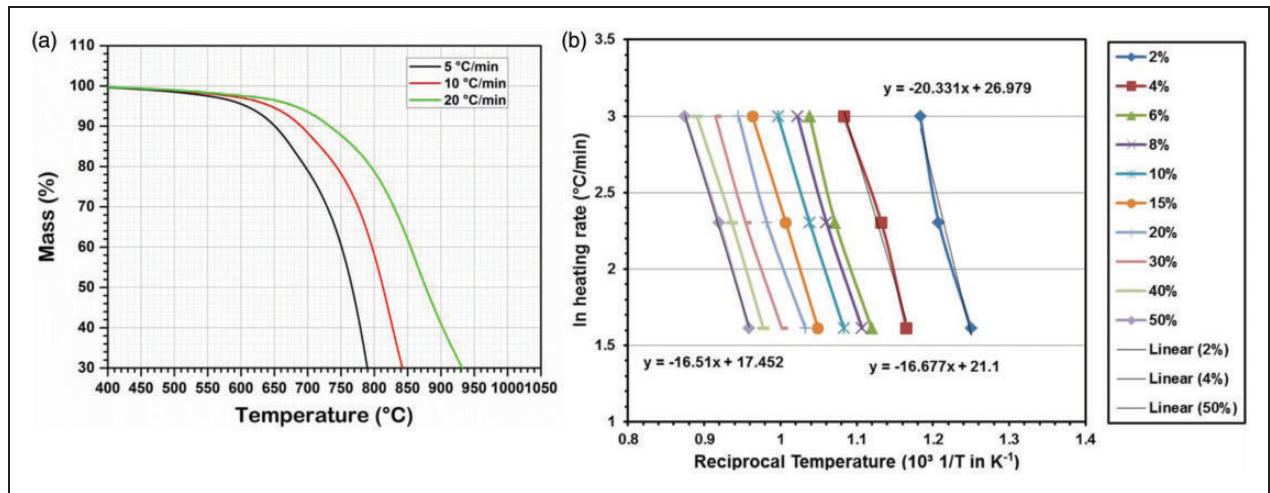

Figure 7. (a) TGA curves with different heating rate and (b) ln heating rate versus reciprocal temperature plots of coated sample C1 up to 50% conversion.

from these results that the activation energies for the thermo-oxidative changes of coated samples are higher up to 50% conversion compared to uncoated CF. The calculated activation energy is 117–128 kJ/mol for up to 50% burn-off of uncoated CF. This activation energy value obtained for uncoated CF is found to be nearly the same as the results available in the literature.[31,32] Remarkably, the highest activation energy (140–160 kJ/mol) is obtained in the case of SiO$_2$ sol–gel coated sample C2. The higher activation energy for the mass loss of the sample C2 may result from the decomposition of organic components, since this sol–gel coating contains a higher portion of organic structural elements. The range of activation energy for the oxidation

of sample C1 is 130–140 kJ/mol from 4% to 50% conversion.

It can be deduced from these results that the activation energy is enhanced by coatings on CF. At lower temperature ranges (450–725°C), an increased value of activation energy is found, which leads to lower oxidation rate. The rapid oxidation is indicated by the accelerated conversion with an increase of temperature (700–880°C). In the case of coated CF samples, the oxidation process at higher temperature ranges is controlled by the chemical reaction and oxygen diffusion through the pore of coatings as well as through the micro crack, which may occur because of thermal expansion mismatch between CF and coatings.

Mechanical and thermo-mechanical properties

Figure 9(a) illustrates the tensile strength (at 20°C, 300°C, 400°C, 500°C, 600°C, 700°C, and 750°C) comparison of uncoated and coated samples. It is obvious that the tensile strength of coated samples C1 and C2 increases, respectively, by 60% and 85% at room temperature (20°C) compared to that of uncoated CF yarn. The increase in strength at room temperature may be attributed to the enhanced bonding among the individual filaments, to the improvement of filament micro friction/adhesion within the yarn, and to the healing of surface defects.

The uncoated CF yarn retains its original strength up to 600°C, which is found from our investigation. However, the strength of the uncoated sample is drastically reduced after thermal-tensile load at 700°C and the strength loss amounts to 60%. This sample loses more than 90% of its strength at 750°C. The drastic loss of tensile strength from 700°C can result from the
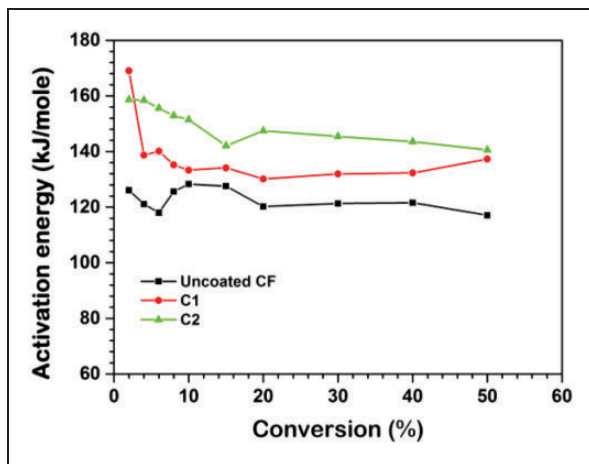

Figure 8. Activation energy comparison of uncoated and coated CF samples up to 50% conversion.
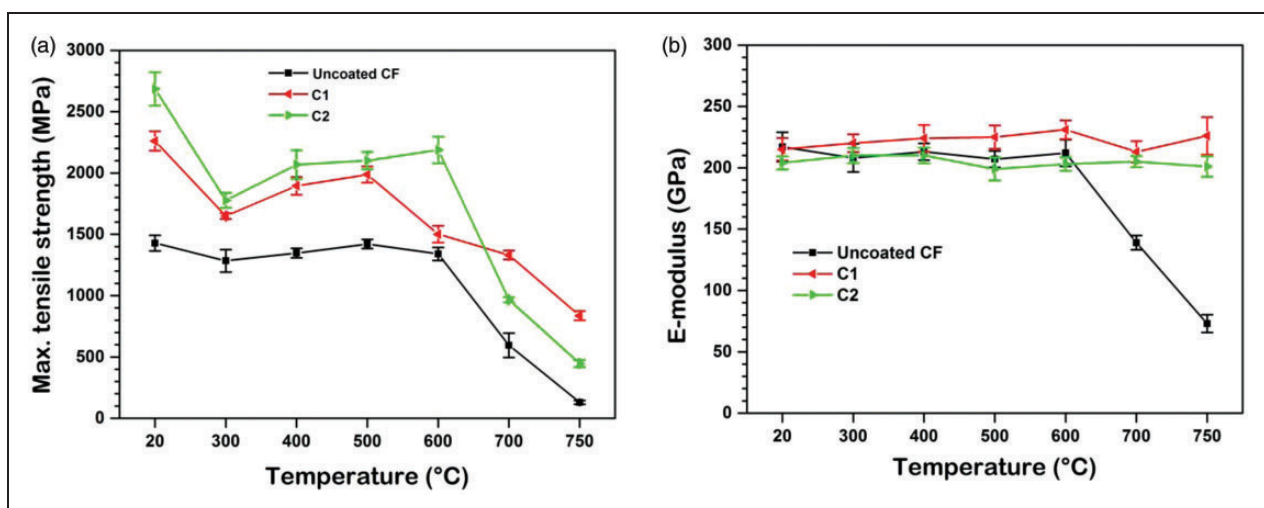

Figure 9. Comparison of (a) tensile strength and (b) E-modulus of uncoated and coated CF yarns with varying temperatures.

changes of supermolecular structure as well as rapid oxidation of CF. In contrast, the samples with thermal and oxidation resistant coatings (C1 and C2) exhibit higher tensile strength compared to the uncoated CF up to 600°C. At 700°C, Tyranno® polymer coated sample C1 maintains the original strength of uncoated CF measured at 20°C. Besides, the strength retention is ca. 70% for the SiO_2 sol–gel coated sample C2 at 700°C. After the thermo-mechanical loading under 750°C, the sample C1 maintains highest 60% strength of uncoated CF yarn. The enhancement of thermo-mechanical properties might be due to the surface healing, improvement of filament–filament adhesion, as well as thermal and oxidation barrier effects caused by the coatings. These coating polymers are crosslinked with each other during heating at high temperatures and form silicon ceramics, which act as a thermal and oxidation barrier on to the CF yarns.

Moreover, the results of elasticity modulus (E-modulus) measurements of uncoated and coated CF yarns are shown in Figure 9(b). The uncoated CF maintain its E-modulus, i.e. the stiffness properties up to 600°C, whereas there is a little or no considerable changes of E-modulus observed for the coated samples during thermo-mechanical loading up to this temperature. However, the uncoated CF losses 35% and 65% of its E-modulus at 700°C and 750°C, respectively. Remarkably, heat and oxidation resistant pre-ceramic coatings (samples C1 and C2) retain E-modulus, i.e. the stiffness of uncoated CF yarn at 700°C and 750°C.

The main purpose of the coating with thermal and oxidation resistant materials was to enhance the thermo-mechanical properties of CF yarn at high temperatures. After the investigation of thermo-mechanical properties of CF yarn, it is found that the tensile strength considerably increases up to 600°C after the coating. At 700°C, the coated sample C1 retains the strength of uncoated CF yarn and up to 60% strength is sustained during testing at 750°C. From the thermo-mechanical results, it can be concluded that the thermal and oxidation resistant coatings not only improve the tensile strength but also retain the E-modulus, i.e. the stiffness of CF yarns up to 750°C. This can be highly advantageous from the CF reinforcement in composite structure viewpoint, especially in terms of the mechanical and thermo-mechanical stress improvements.

Relationship between the tensile strength and mass loss based on TGA. Tensile testing of the samples was conducted in ambient air at room temperature (20°C), 300°C, 400°C, 500°C, 600°C, 700°C, and 750°C. TGA was carried out from 30°C to 1000°C in ambient conditions. Figure 10 (left y-axis and right y-axis show the actual mass loss percentage and measured tensile strength, respectively) clearly shows that the primary weight loss up to 600°C
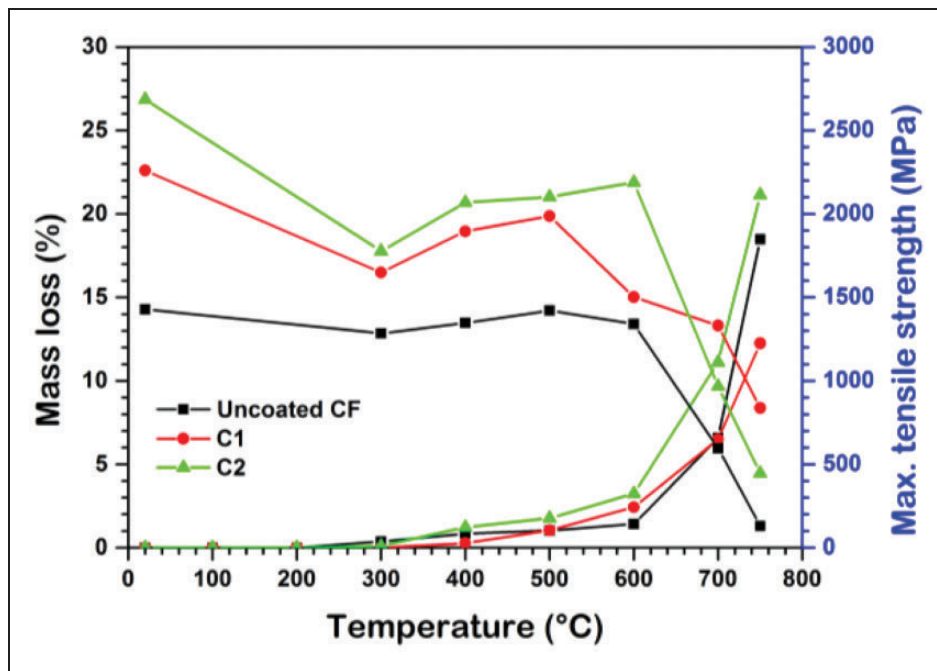
Figure 10. Relationship between the tensile strength and mass loss of uncoated and coated CF yarns based on TGA data at ambient condition.

has no considerable influence on tensile strength of uncoated CF yarns. The uncoated CF loses, respectively, 6.60% and 18.50% mass at 700°C and 750°C during the TGA at ambient air condition; however, it loses nearly 60% and more than 90% of its strength after thermal-tensile loading at those temperatures. The possible reasons for the drastic loss in tensile strength under thermal loading at high temperatures (from 700°C) in ambient conditions may be the changes in the internal structure as well as the oxidation mass loss of uncoated CF. Instead, the reduction of mass is 6.5% at 700°C in the case of coated sample C1, but nevertheless it retains the original strength of the CF yarn at the same temperature. At 750°C, the decline in mass is 12.25% for the sample C1 and the strength retention amounts to 60%. The enhancement and retention of strength at high temperature may be explained in terms of the oxidation protection through the ceramic layer of coated samples. It can be concluded from this discussion that the tensile strength is enhanced and the oxidation of CF is restricted by thermal and oxidation resistant coatings. Tyranno® polymer coated sample C1 shows better thermal and thermo-mechanical properties compared to SiO_2 sol–gel coated sample C2.

Conclusion

The results of our study indicate that the topographical, thermal and oxidation stability, as well as thermo-mechanical properties of CF can be considerably improved by Si and Si–Ti based pre-ceramic coatings. SEM, XPS, and IR-spectroscopy analysis clearly revealed that the surface microstructure and chemical compositions of CF changed due to the deposition of the coatings. The results of TGA indicated that the Tyranno® polymer (C1) coating exhibited higher thermo-oxidative stability up to 800°C compared to uncoated CF. Besides, it revealed improved oxidation stability during isothermal TGA at 500°C, 600°C, and 700°C. The activation energy for the oxidation process of CF is enhanced by the coatings. Investigation of the thermo-mechanical properties revealed that the tensile strength of coated samples increased by up to 80% depending on coatings compared to that of uncoated CF yarn at room temperature (20°C). Tensile strength was also enhanced considerably under thermal and tensile load up to 600°C due to the coatings. At 700°C, the uncoated CF yarn lost 60% of its strength, whereas Tyranno® polymer coated sample C1 retained the strength of uncoated CF yarn measured at 20°C. The strength loss was more than 90% at 750°C for uncoated CF yarn, while the coated sample C1 retained about 60% of its strength at that temperature. It has been also found that the applied thermal and oxidation resistant coatings not only improved the tensile strength but also retained the E-modulus, i.e. the stiffness of CF yarns, up to 750°C.

Finally, a conclusion can be drawn based on the obtained results of this study that the potential of Tyranno® polymer coating for the protection of CF from the thermal oxidation and the improvement of thermo-mechanical properties is very high and could be advantageous for the continuous fiber reinforcement in composites, especially textile-reinforced concrete structures for high temperature application. As a consequence, textile-reinforced concrete composites can satisfy the high level of fire resistant standards. The results of this study can play an important role for further investigations of such coatings in fire resistant textile reinforced concrete composites for the replacement of steel. The results achieved from the research can be used for other fire protective textile applications, e.g. flame protective linings.

Declaration of conflicting interests

Funding

References

1. Outinen J and Mäkeläinen P. Mechanical properties of structural steel at elevated temperatures and after cooling down. In: *2nd international workshop of structures in fire*, Christchurch, New Zealand, March 2002.
2. Younes A. *Experimental analysis and modeling of mechanical behavior of high performance fiber materials under long term load, high temperature and impact for composites applications*. PhD Thesis, Technische Universität Dresden, Germany, 2013.
3. Manocha LM. High performance carbon–carbon composites. *Sadhana* 2003; 28: 349–358.
4. United Composites. High temperature performance composites, www.unitedcomposites.net/usapages/hightempperformancecomposites2.htm (accessed 28 May 2014).
5. Bill J and Heimann D. Polymer-derived ceramic coatings on C/C–SiC composites. *J Eur Ceram Soc* 1996; 16: 1115–1120.
6. Papakonstatinou CG, Balaguru P and Lyon R. Comparative study of high temperature composites. *Composites Part B* 2001; 32: 637–649.
7. Hund H and Hund RD. Textile Ausrüstung und Ausrüstungstechniken. In: Cherif C (ed.) *Textile Werkstoffe für den Leichtbau*. Berlin: Springer Verlag, 2011, pp.462–464.

8. Baklanova NI and Zima TM. Barrier coating of carbon and carbide silicon fibers for composites with ceramic matrix. *Chem Sustainable Dev* 2006; 14: 223–226.

9. Kim BH, Kim SY, et al. Preparation of anti-oxidative carbon fiber at high temperature. *Appl Surf Sci* 2010; 257: 662–664.

10. Hatta H, Aoki T, et al. High-temperature oxidation behavior of SiC-coated carbon fibre reinforced carbon matrix composites. *Composites Part A* 1999; 30: 515–520.

11. Wang Y-Q, Zhou B-L and Wang Z-M. Oxidation protection of carbon fibres by coatings. *Carbon* 1995; 33: 427–433.

12. Kawai C and Igarashi T. Oxidation-resistant coating of TiC–SiC system on carbon/carbon composite by chemical vapor deposition. *J Ceram Soc Jpn* 1991; 99: 377–381.

13. Park SJ and Cho MS. Effect of anti-oxidative filler on the interfacial mechanical properties of carbon–carbon composites measured at high temperature. *Carbon* 2000; 38: 1053–1058.

14. Xia KD, Lu CX and Yang Y. Preparation of anti-oxidative SiC/SiO_2 coating on carbon fibers from vinyl-triethoxysilane by sol–gel method. *Appl Surf Sci* 2013; 265: 603–609.

15. Yun J, Choi Y and Lee H. Crack-healing capability and high temperature oxidation resistance of multilayer coatings for carbon-carbon composites. *J Ceram Process Res* 2009; 10: 340–343.

16. Colombo P, Mera G, et al. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. *J Am Ceram Soc* 2010; 93: 1805–1837.

17. Greil P. Polymer derived engineering ceramics. *Adv Eng Mater* 2000; 2: 338–348.

18. Kern F and Gadow R. Liquid phase coating process for protective ceramic layers on carbon fibers. *Surf Coat Technol* 2002; 151–152: 418–423.

19. Bauer F, Decker U, et al. Preparation of moisture curable polysilazane coatings. Part I. Elucidation of low temperature curing kinetics by FT-IR spectroscopy. *Prog Organ Coat* 2005; 53: 183–190.

20. KiON Corp. Technical bulletins, KiON® polysilazane, www.kioncorp.com/bulletins/ (accessed 12 January 2014)

21. Shayed MA, Hund RD and Cherif C. Polysilazane based heat and oxidation resistant coatings on carbon fibers. *J Appl Polym Sci* 2012; 124: 2022–2029.

22. Hashishin T, Murashita J, et al. Oxidation resistant coating of carbon fibers with TiO_2 by sol–gel method. *J Ceram Soc Jpn* 1998; 106: 1–5.

23. Young SK. Sol–gel science for ceramic materials. *Mater Matters* 2006; 1: 8–13.

24. Shayed MA, Hund RD and Cherif C. Effect of thermal resistant polymeric coatings on thermomechanical and topographical properties of glass fiber. *J Ind Text* 2015; 45: 682–698.

25. Flynn JH and Wall LA. A quick, direct method for the determination of activation energy from thermo gravimetric data. *Polym Lett* 1966; 4: 323–328.

26. Ozawa T. Estimation of activation energy by isoconversion method. *Thermochim Acta* 1992; 203: 159–165.

27. Doyle CD. Kinetic analysis of thermogravimetric data. *Appl Polym Sci* 1961; 5: 285–293.

28. Wangxi Z, Jie L and Gang W. Evolution of structure and properties of PAN precursors during their conversion to carbon fibers. *Carbon* 2003; 41: 2805–2812.

29. Polmanteer KE. New developments in silicone elastomers. *J Elastoplast* 1970; 2: 94–165.

30. Dvornic PR. Thermal stability of polysiloxane. In: Arkles B and Larson G (eds) *Silicon Compounds: Silanes and Silicones, a Survey of Properties and Chemistry*, 2nd ed. Morrisville, PA: Gelest Inc, 2008, pp.441–454.

31. Tong Y, Wang X, et al. Oxidation kinetics of polyacrylonitrile-based carbon fiber in air and the effect on their tensile properties. *Corros Sci* 2011; 53: 2484–2488.

32. Yin Y, Binner JGP, et al. The oxidation behavior of carbon fibres. *J Mater Sci* 1994; 29: 2250–2254.