

Polysilazane-Based Heat- and Oxidation-Resistant Coatings on Carbon Fibers

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ABSTRACT: Carbon fibers must be protected from a high-temperature oxidizing environment because, at approximately 500°C and above, the fibers exhibit reduced mass and strength stability. The fibers can be protected by the application of thermal coatings, which simultaneously improve the adhesive properties of the carbon fibers in the composite materials. Polysilazanes are a new family of heat-resistant polymer coatings that are converted into silicone carbide or silicone nitride ceramic structures at high temperatures. The converted ceramics are resistant to the effects of high temperatures. In this research work, polysilazane-based coatings were applied to carbon filament (CF) rovings with the dip-coating method. Tensile testing

at room temperature and under thermal stress was carried out to assess the mechanical and thermomechanical properties of both coated and uncoated rovings. Scanning electron microscopy and energy-dispersive X-ray analysis were performed to evaluate the surface topographical properties of the coated and uncoated rovings. Thermogravimetric analysis was executed to determine the thermal stability of the polymer coatings. The coating performance on the CF rovings was determined by assessment of the test results obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2022–2029, 2012

Key words: coatings; fibers; thermal properties

INTRODUCTION

Currently, heat- and oxidation-resistant coatings for carbon fibers are a highly interesting subject of research for scientists worldwide and are extremely relevant for practical composite applications. Studies conducted on heat-resistant coatings for textiles continue to increase with the aim of developing new functional properties for textile materials and diversifying complex textile applications.^{1,2} Along with other coatings, polysilazane-based polymers used as heat-, oxidation-, and corrosion-resistant coatings in ceramic or metal matrix composites have been intensively researched in recent years.^{2–5} These polymers are converted to silicon carbide or silicon nitride ceramic structures at elevated temperatures.⁵ Carbon fibers need to be protected by stable and effective ceramic coatings when they are exposed to oxidative or chemically aggressive environments during composite manufacturing and subsequent applications. Additionally, the coatings should provide micro and mechanical protection, enhance the shear stability, increase the bonding strength at the interface of the

fiber and the matrix, and reduce friction for optimum mechanical properties and fracture toughness.⁶

Because of its light weight, high specific strength, and Elasticity modulus, carbon fibers are being used increasingly in the area of textile-reinforced concrete and fiber-reinforced plastics in the aerospace industry, electrical and electronic industries, automotive sector, mechanical engineering, and in sport textiles, protective textiles, and so on.^{7,8} Despite the excellent physical and chemical properties of carbon fibers, they have also limitations. The major problem is their low stability in atmospheres with elevated temperatures and those containing oxygen.⁹ Such conditions result in reduced thermomechanical properties. Under normal conditions, carbon fibers remain intact up to 400°C.¹⁰ In addition, the surface of the carbon fiber is highly inert, which affects the chemical interactions at the fiber–matrix interface and, thus, negatively influences the mechanical properties of the composite. To overcome these restrictions, new heat-resistant coatings are being developed to improve the high-temperature stability and protect against oxidation of the fibers. The oxidation of carbon fibers can be prevented by heat-resistant coatings, as shown by Hatta et al.,¹¹ who used a ceramic coating to protect carbon fibers against thermal degradation.

The improvement of current textile properties, the creation of new material properties, and the protection of materials from extreme environmental attack are the most important reasons for coating textiles. In contrast to the moderate growth of conventional

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textiles, functional high-grade textiles show overproportional market growth. The functional coating of textile materials enables considerable improvements in the performance and durability of technical textiles (e.g., in composites, the automotive field, protective textiles, railroad and aerospace engineering, construction, and home textiles).^{12–16} Additionally, the coating of textiles with functional layers is an indispensable process for meeting growing requirements for technical textiles.¹⁶ Thermal-resistant coatings based on polysilazane polymers facilitates the modification of textile materials with improved properties, so polysilazane coatings on carbon filament (CF) rovings will enable new advantageous functions for high-temperature applications.

The main objectives of this study were the application of thermal coatings on CF rovings and the characterization of the coated rovings. To fulfill these objectives, a polysilazane polymer was applied to CF rovings by means of the dip-coating method. Then, the surface topography and thermal and tensile properties of the coated samples were investigated through different experiments. Upon completion, the testing results were assessed to determine the coating performance as thermal protection for textiles.

EXPERIMENTAL

Materials

Textile materials

Toho Tenax CF roving Tenax-E HTS40 F13, with 800 tex and with 12,000 filaments in each roving (filament diameter = 7 μm), was used as the substrate for coating in this study. It was supplied by the producer Toho Tenax Europe GmbH (Wuppertal, Germany). The carbon roving was used as received from the producers, that is, without removal of the sizing materials. Polyurethane-based sizing material, which was not thermally stable, was used on the carbon roving.

Coating material

Polysilazane type KiON HTT 1800 was a heat-curable, high-temperature resin. It was supplied by Clariant GmbH (Frankfurt am Main, Germany). It was a low-viscosity liquid and was clear to slightly yellowish.

Solvent

Acetic acid ester was supplied by Biesterfeld (Hamburg, Germany). It was a low-viscosity liquid and was colorless.

Coating procedure and working principle

Coatings of textile fibers, rovings, or fabrics can be applied by different methods or techniques,¹⁷ which

depend on the type of substrates and coating materials. The coating polymer was applied to the CF roving with the dip-coating method. The coating experiment was carried out with a Coatema Basecoater BC32 (Coatema Coating Machinery GmbH, Dormagen, Germany). The chemistry of the polysilazane coating is shown in Figure 1.

At first, a homogeneous coating liquor was prepared by the dissolution of polysilazane into the acetic acid ester solvent according to the respective recipe under constant stirring and was then put into the dipping bath. The CF roving was impregnated or dipped in the dipping bath at a speed of 0.5 m/min and then passed over the roller without squeezing; it was then dried at 205°C in a drying unit. Subsequently, the roving was wrapped continuously on the delivery roller. The percentage coating on the roving was determined by the weights of the sample before and after coating.

The coating recipes, parameters, and percentages are illustrated in Table I.

Surface characterization

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis

The evaluation of the changes in the surface topography of the coated samples was done by SEM (Zeiss DSM Gemini 982, Oberkochen, Germany). There was an additional detector with the SEM instrument to identify surface elements.

Thermogravimetric analysis (TGA)

TGA was performed to investigate the weight losses and thermal stability of samples in air and in an N₂-containing atmosphere. TGA was carried out with a TA Instruments Q500 (Grimsby, ON, L3M4E7, Canada) within the temperature range 25–940°C in air or N₂ at a flow rate of 60 mL/min and at a 10°C/min heating rate. In this TGA experiment, a vertical-type analytical balance was used to record the weight change.

Tensile testing

The tensile strengths of the coated and uncoated CF rovings were measured to assess the coating effect on

TABLE I
Coating Recipes, Parameters, and Percentages

Recipe	Polysilazane/ ester weight ratio	Speed (m/min)	Drying temperature (°C)	Coating (%)
1	1 : 11	0.5	205	3.03 ± 0.23
2	1 : 7	0.5	205	8.11 ± 0.80

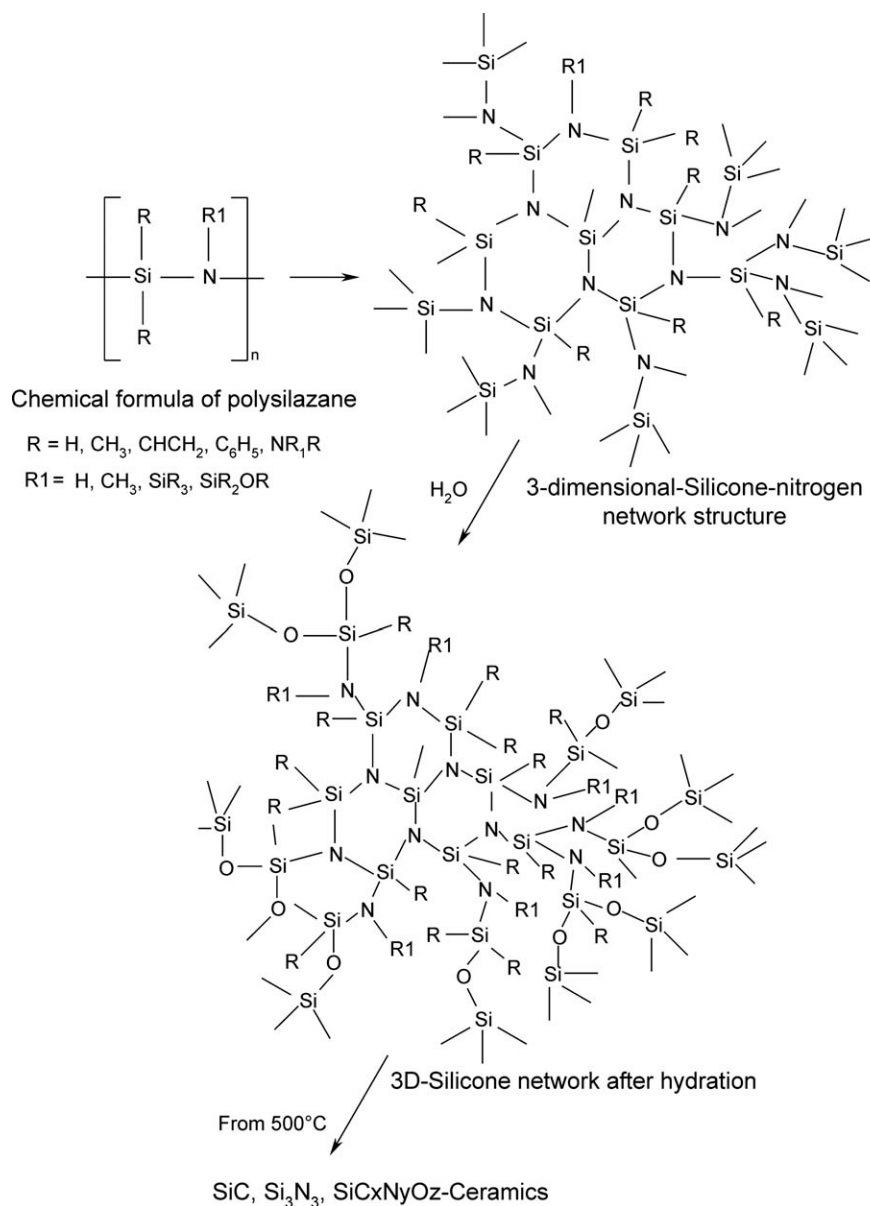


Figure 1 Chemistry of coating with polysilazane.

the mechanical properties of the roving. The test was performed according to test standard ISO 3341 at a temperature of $20 \pm 2^\circ\text{C}$ and at $65 \pm 2\%$ relative humidity, with a Zwick material testing machine (type Z 100, Ulm, Germany), having special return clamps, external strain measuring equipment, and IR heating equipment, with a vacuum system to introduce thermal stress on roving. The stress-strain behavior was measured with testXpert software (Zwick, Ulm, Germany). The test was carried out at room temperature and under thermal stress at 300, 400, and 450°C . The sample was heated at $20^\circ\text{C}/\text{min}$ with the IR heating system for thermal loading, where the temperature sensor measured the sample temperature. A test sample was clamped vertically with upper and lower clamps.

After the sample was clamped, the initial load was kept at 0.5 cN/tex. Then, the test was started with a preset speed of 200 mm/min, and stretching was continued until breakage. The results of the breaking force (newtons), strength (newtons per square millimeter), E modulus (gigapascals), and the elongation (percentage) were registered for each measurement with the testXpert software. Each test was repeated five times to ensure accurate results.

RESULTS AND DISCUSSION

SEM analysis

SEM views of the coated and uncoated CF rovings showed changes in the surface characteristics. The

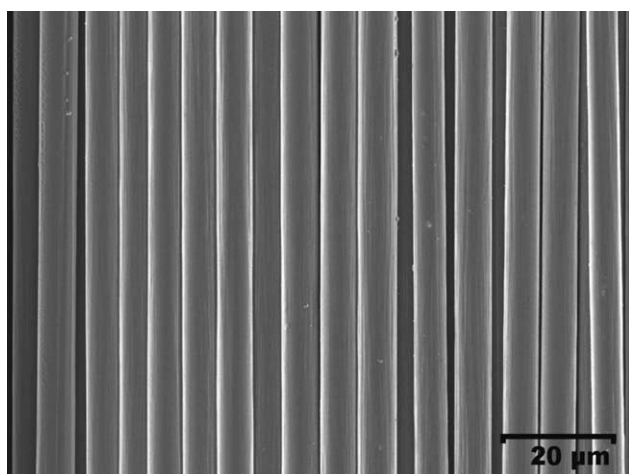


Figure 2 SEM views of uncoated CF rovings.

surface properties of different samples were easily identified from the SEM views enlarged 1000 times. The surface SEM micrographs of the uncoated and coated CF filaments are shown in Figures 2–4. The SEM picture of the uncoated CF showed a relatively smooth and homogeneous surface. The particles of the primary sizing materials aggregated very lightly on the surface of the uncoated CF (Fig. 2).

The sample coated with recipe 1 (R1) showed a smooth and very thin coating layer on the surface; this showed that the coating percentage for this sample was the lowest (Fig. 3). SEM images of the sample coated with recipe 2 (R2) revealed a relatively homogeneous and smooth coated surface of CF roving, as shown in Figure 4. There was no significant difference to be found between the SEM views of the uncoated and coated CF rovings, as the polysilazane coating was transparent, but the individual CF filaments were bridged together by coatings in all of the coated samples, which are shown as the distinguishing feature.

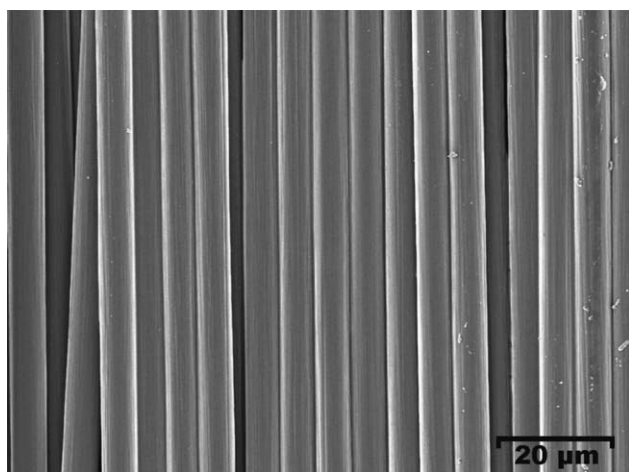


Figure 3 SEM views of CF rovings coated with recipe 1.

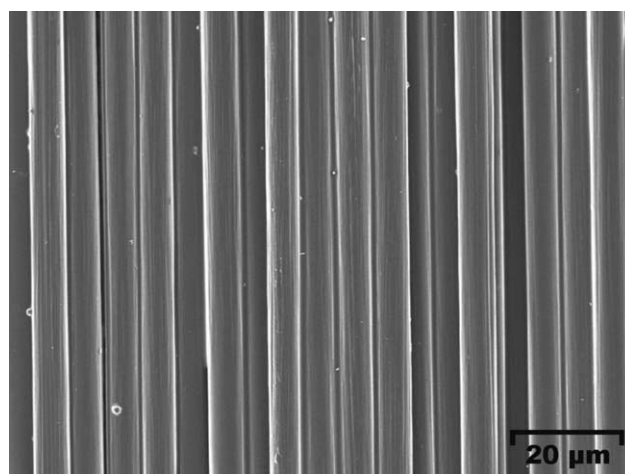


Figure 4 SEM views of CF rovings coated with recipe 2.

EDX analysis

In EDX analysis, the energy and wavelength of the X-ray emitted from the atoms of the specimen is attributed to the elements of the parent atoms. The X-rays emitted, because they are characteristic of the atomic structure of the element from which they were emitted, can be used to identify and quantify the elements. EDX was performed on the uncoated and coated samples to evaluate the chemical changes in the samples for a semiquantitative identification of the chemical compositions. EDX spectra were taken from different areas of the coated and uncoated CF filaments (Table II). We observed that the uncoated CF contained nearly 100% carbon atoms.

In contrast, the coated samples contained carbon, silicon, oxygen, and nitrogen as their main elements. From the EDX data of the coated CF samples, it is clearly shown that oxygen, silicon, and nitrogen atoms (in weight percentage) were added on the CF surface from the polysilazane coatings. The nitrogen atom was not detected during the EDX experiment, but the atomic percentage was still calculated.

TGA results

The oxidation behavior and thermal decomposition of the coated and uncoated CF samples were

TABLE II
EDX Data of the Coated and Uncoated CF Rovings

Sample	Element	Atom %	Elemental wt %
Uncoated CF	C	99.88	98.15
R1	C	99.49	99.20
	Si	0.18	0.41
	N	0.33	0.39
R2	C	96.93	95.91
	O	0.11	0.15
	Si	0.46	1.07
	N	2.50	2.88

TABLE III
Weight Loss Percentages at Different Temperature Stages in Ambient Air (According to the TGA Data)

Sample	Weight loss (%) at					
	400°C	500°C	600°C	700°C	750°C	800°C
Uncoated CF	2.55	2.77	3.50	17.80	62.11	98.84
R1	0.99	1.18	1.80	17.30	40.79	87.79
R2	0.98	1.28	2.11	18.35	40.45	84.75

investigated with TGA. The TGA results of the uncoated and coated samples are illustrated in Table III and Figures 5 and 6. The experiment was carried out under ambient air and an N_2 atmosphere up to $940^\circ C$. The uncoated and CF samples R1 and R2 showed thermal stability in the inert N_2 atmosphere up to $940^\circ C$ with minimum weight loss in this case. It was observed that the weight losses were 2.2 and 1.2–1.5% for the uncoated and coated samples, respectively (Fig. 5). This weight loss could be accounted for by the removal of the primary sizing material from the uncoated sample, which amounted to about 1%, and the removal of volatile oligomers from the coated samples. On the contrary, when the uncoated CF sample was heated under air flow, it underwent strong oxidation and weight loss. This sample started to oxidize at about $300^\circ C$ at a somewhat slower rate; this increased to rapid oxidation above $500^\circ C$. For this specimen, the weight losses were 3.5, 17.80, 62.11, and more than 98% at 600, 700, 750, and $800^\circ C$, respectively (Table III, Figs. 5 and 6).

In contrast, the coated CF samples began to oxidize at $500^\circ C$ at a slower oxidation rate than that of the uncoated sample, with rapid oxidation occurring above $700^\circ C$. This may have been due to the formation of a ceramic layer on the surface or a reduction in the porosity of the polysilazane coating by the for-

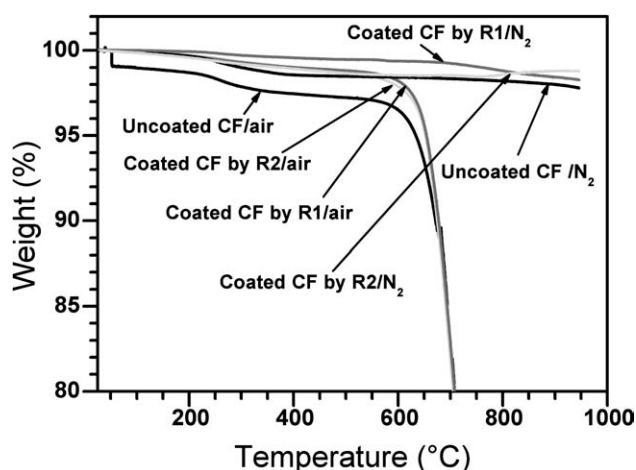


Figure 5 TGA curves of the initial weight changes of coated and uncoated CFs under N_2 and ambient air.

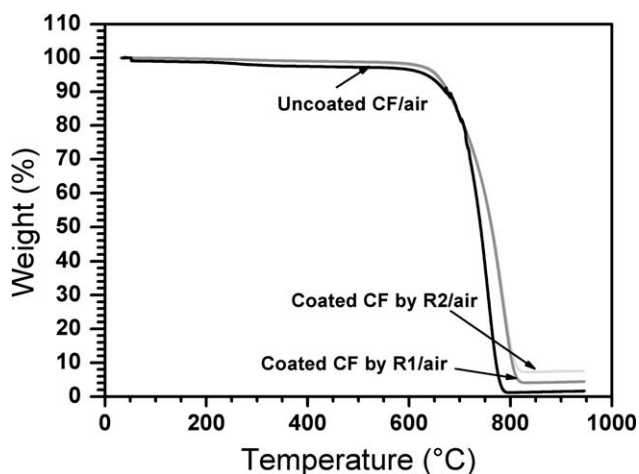


Figure 6 Full TGA curves of the coated and uncoated CFs in ambient air.

mation of silicon dioxide, which led to a lower diffusion rate of oxygen through the pores.⁹

From the TGA traces of the specimens under ambient air, we observed that up to $650^\circ C$, the weight loss was less for the coated samples. The weight loss in these samples up to $650^\circ C$ was attributed to the decomposition of the polymeric material and the volatile oligomers in the coating material. The major weight loss occurred between 700 and $800^\circ C$. Both the samples R1 and R2 lost approximately 40% of their original weight at $750^\circ C$ in ambient air.

The weight loss was found to be more than 80% for both of the coated samples at $800^\circ C$. It was clearly seen that the major weight loss occurred between 750 and $800^\circ C$. The reasons for the weight loss were the porosity of the layer and some microcracks (Fig. 7), which may have developed during

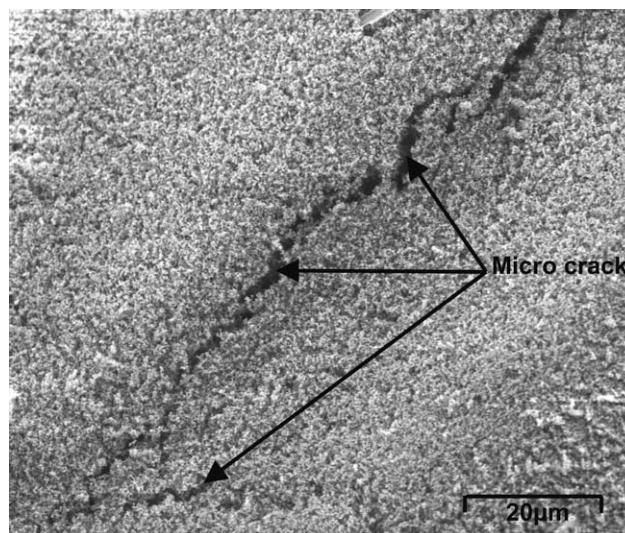


Figure 7 SEM image of microcracks on the polysilazane-coated samples after heating at high temperature in ambient air.

TABLE IV
Tensile Testing Data at Different Temperatures

Sample	Temperature (°C)	Breaking force (N)	Tensile strength (N/mm ²)	E modulus (GPa)	Elongation (%)
Uncoated CF	20	785 ± 64.90	1756.44 ± 145.21	171 ± 14.80	0.96 ± 0.07
	300	713 ± 28.3	1595.34 ± 63.32	189 ± 9.38	0.92 ± 0.09
	400	379 ± 32.40	848.01 ± 72.50	156 ± 13.30	0.71 ± 0.10
	450	0	0	0	0
R1	20	1090 ± 84.60	2438.88 ± 189.21	181 ± 11.40	1.18 ± 0.08
	300	833 ± 70.90	1863.84 ± 158.64	183 ± 12.10	0.91 ± 0.09
	400	584 ± 59.10	1306.70 ± 132.24	159 ± 10.80	0.74 ± 0.07
	450	75.8 ± 2.71	169.60 ± 6.06	83.30 ± 12.50	0.24 ± 0.02
R2	20	1270 ± 22.20	2841.63 ± 49.67	175 ± 10.10	1.33 ± 0.03
	300	917 ± 26.20	2051.79 ± 58.62	173 ± 9.14	1.03 ± 0.03
	400	602 ± 61.30	1346.98 ± 137.16	165 ± 8.09	0.74 ± 0.06
	450	73.6 ± 18.40	164.68 ± 41.17	—	0.20 ± 0.02

the heating. The cracks were caused by a difference in the thermal expansion coefficients of the carbon fiber and the coating material. Consequently, it was proven that the coated samples showed better TGA results than the uncoated specimens. We concluded that the thermal stability of the carbon fiber was improved by the polysilazane coating.

Tensile test results

The tensile strength and stress–strain behavior of the uncoated and coated specimens were investigated at room temperature (20°C) and under thermal stress at 300, 400, and 450°C. The data of tensile testing is reproduced in Table IV, and the tensile strength comparison of the uncoated and coated CF samples depending on temperature is illustrated in Figure 8. O-CF represents the uncoated sample.

At room temperature, both the coated CF samples showed an increase of 40–60% in strength over the uncoated CF samples. Furthermore, the strength of the coated CF samples R1 and R2 increased by about

20–30% over their original strength when they were heated to 300°C. At 400°C, the strength showed increases of about 55 and 60% for the coated CF samples R1 and R2, respectively, as compared to the uncoated sample at that temperature. The uncoated sample wore out completely at 450°C, whereas the coated CF samples did not experience breakdown under thermal and tensile loads in those conditions. The main cause for the increase in tensile strength was the improvement in the filament–filament friction/adhesion within the roving. Therefore, we concluded that the modification of CF roving with a heat-resistant coating led to an increase in the tensile strength under thermal loads due to the thermal barrier coating protecting the carbon fiber from oxidation and generally improving its thermal stability.

Additionally, typical stress–strain properties were analyzed during tensile testing at different temperatures. The stress–strain curves of the uncoated and coated CF rovings are illustrated in Figures 9, 10, and 11.

The curves exhibited a linear pattern until the critical load was reached at room temperature for both the coated and uncoated samples. However, under

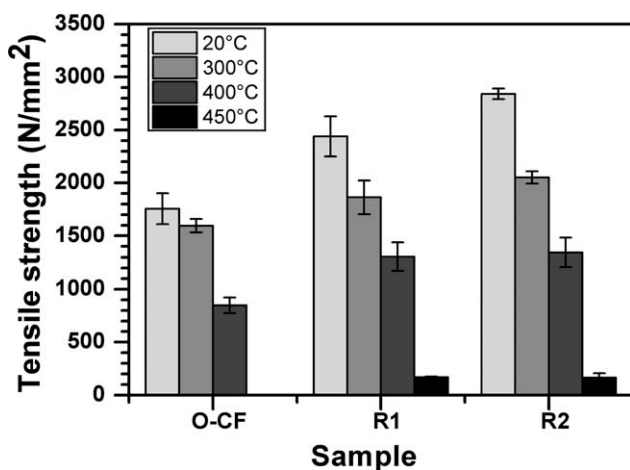


Figure 8 Tensile strength of the uncoated and coated CF rovings depending on temperature.

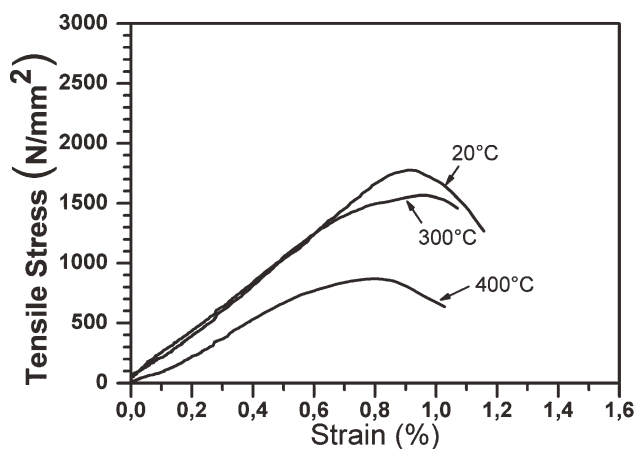


Figure 9 Stress–strain curves of uncoated CF rovings.

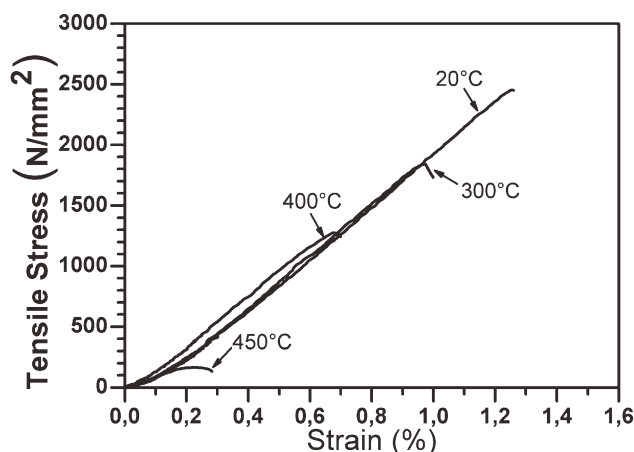


Figure 10 Stress–strain curves of CF rovings coated with recipe 1.

thermal loads of 300 and 400°C, the curves became nonlinear until the ultimate breaking point for the uncoated CF was reached. At these temperatures, the coated samples continued to exhibit almost linear curves. Breakage or failure occurred at the critical load, except in the stress–strain curve at 300°C of sample R2. Because of the partial breakage of filaments, this sample showed increasing strain and decreasing stress after the critical loading. Because of the different linear thermal expansion coefficients between the CF and the coating material, the stress–strain behaviors were also different in the case of the uncoated and coated samples. The stress–strain curves revealed that the tensile E modulus, that is, the stiffness, of the coated samples was higher than that of the uncoated sample at 300 and 400°C. It could be deduced clearly from the tensile test results that the modification of the CF roving by polysilazane-based thermal coatings not only improved the tensile strength but also changed the stress–strain behavior, that is, the stiffness, of the filament roving.

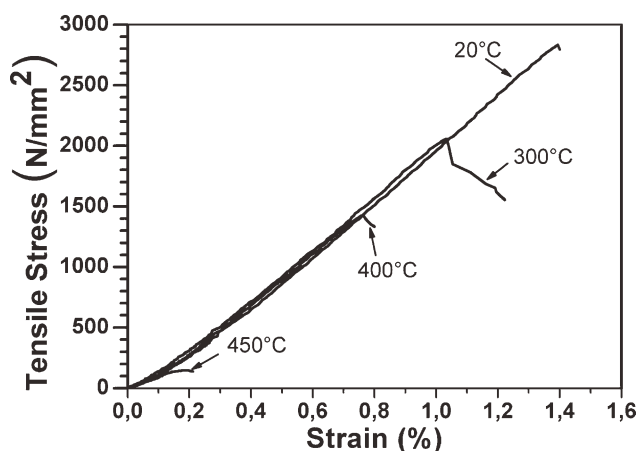


Figure 11 Stress–strain curves of CF rovings coated with recipe 2.

Relationship between the weight loss on the basis of TGA and tensile strength

Tensile testing of the samples was conducted in ambient air at room temperature and 300, 400, and 450°C. TGA was carried out from 20 to 940°C in ambient conditions. Figure 12 (the left y -axis scale shows the actual weight loss percentage, and the right y -axis scale measures the tensile strength) clearly shows that the weight loss was less for both the coated and uncoated samples up to 600°C. However, under tensile loading, they could not sustain their strength at this temperature. At 300°C, the weight loss of the uncoated sample was 2.10%, a 10% reduction from its original strength.

On the contrary, the weight loss of the coated samples was 0.70%, and the strength increased by approximately 15% under similar temperature conditions as compared to the uncoated sample. The uncoated sample lost only 2.50 and 2.70% of its weight at 400 and 450°C, respectively, during TGA at ambient conditions, but it lost about 50% of its strength at 400°C and completely wore out during tensile testing at 450°C; that is, the tensile strength was zero. On the other hand, the coated samples lost approximately 1 and 1.10% of their weight at 400 and 450°C, respectively, but they retained about 75 and 10% of the original CF roving strength at those temperatures. The possible reasons for the drastically loss in the tensile strength under thermal loading at high temperatures in ambient conditions might have been the changes in the internal structure of the carbon fiber during oxidation and the formation of oxidation byproducts at high temperatures. We concluded that the tensile strength and thermal stability of the carbon fiber were improved by the polysilazane coating.

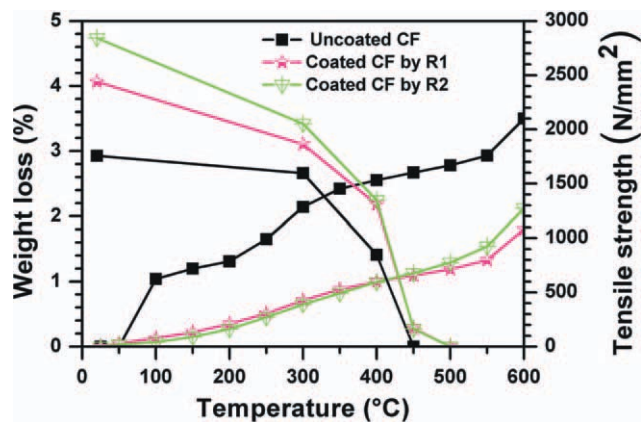


Figure 12 Relationship between the tensile strength and weight loss of the coated and uncoated CF rovings on the basis of TGA data under ambient conditions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

CONCLUSION AND OUTLOOK

Polysilazane polymer based thermal protective coatings were successfully applied to CF rovings by means of the dip-coating method with different recipes. SEM and EDX results distinguished differences in the morphological properties and the chemical compositions of the surfaces of the coated and uncoated samples. The selected coating improved the thermal stability and thermomechanical and mechanical properties of the carbon fiber. After investigation of the tensile properties at room temperature and under thermal stress, it proven clearly that the coated CF samples exhibited better tensile strength and stiffness compared to the uncoated sample. For example, in some cases, the tensile strength of the coated samples was increased by 50–80% of their original strength. According to the TGA results, the thermal stability and the oxidation protection of the coated samples in ambient air at temperatures up to 800°C were much higher than those of the uncoated sample. However, further study is required to optimize of the coating process and recipe formulations and to observe the effect of nanoadditives on heat-resistant coatings.

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References

1. Shayed, M. A.; Cherif, C.; Hund, R. D.; Cheng, T.; Osterod, F. *Text Res J* 2010, 11, 1118.
2. Shayed, M. A. Master's thesis, Technische Universität Dresden Germany, 2008.
3. Kern, F.; Gadow, R. *Surf Coat Tech* 2002, 151, 418.
4. Bauer, F.; Decker, U.; Dierdorf, A.; Ernst, H.; Heller, R.; Liebe, H.; Mehnert, R. *Prog Org Coat* 2005, 53, 183.
5. KiON Specialty Polymers. Technical Bulletins: KiON Polysilazane. <http://www.kioncorp.com/bulletins/> (accessed 12 August 2009).
6. Gadow, R.; Kern, F. *Adv Eng Mater* 2003, 5, 11.
7. Schneider, M.; Wohlmann, B. *J Text Usage Tech* 2008, 67, 22.
8. Toho Tenax. Applications of Carbon Fibre. <http://www.tohotenax-eu.com/en/products/whats-carbon-fiber/application2009ns.html> (accessed 20 September 2009).
9. Bill, J.; Heimann, D. *J Eur Ceram Soc* 1996, 16, 1115.
10. Papakonstatinou, C.; Balaguru, P.; Lyon, R. *Compos B* 2001, 32, 637.
11. Hatta, H.; Aoki, T.; Kogo, Y.; Yarii, T.; Compos A 1999, 30, 515.
12. Plonka, R.; Mäder, E.; Rothe, C.; Köckritz, U.; Waldmann, M.; Klug, P. *J. Tech Text* 2005, 3, E161.
13. Mahltig, B.; Haufe, H.; Böttcher, H. *J Mater Chem* 2005, 15, 4385.
14. Glawe, A. Coatema Company Presentation; Dresdener Textiltagung; Dresden, Germany, 2006.
15. Giessmann, A. *Substrat- und Textilbeschichtung Praxiswissen für Textil-, Bekleidungs- und Beschichtungsbetriebe*; Springer-Verlag: Berlin, 2003; Chapter 1.
16. Glawe, A.; Giessmann, A. *J Text Excell* 2007, 11, 30.
17. Sen, A. K. *Coated Textiles: Principles and Applications*, 2nd ed.; CRC: Boca Raton, FL, USA, 2008; Chapter 3.