

# Acid Treatment of Carbon Fiber Surface

Rida Gallyamova<sup>1\*</sup>, Vladimir Dokichev<sup>1</sup> and Fanil Musin<sup>1</sup>

<sup>1</sup>Ufa Institute of Chemistry UFRS RAS, 450054, Ufa, Russia

**Abstract.** The paper describes the modification conducted for the PAN carbon fiber surfaces in the solutions of nitric and sulphuric acids. The authors studied the impact of modification parameters such as temperature, acid concentration, time and ratio of the nitrosulphuric acid on the occurrence of reactive groups on the fiber surface. The authors revealed the presence of carboxylic and ketone reactive groups in the range of 1663-1798 and 1568  $\text{cm}^{-1}$  in the IR spectra of carbon fibers. The use of the nitrosulphuric acid did not identify sulfur-containing functional groups on the carbon fiber IR spectra. Preliminary acid treatment of the carbon fiber surface led to the formation of uniform continuous coating of a  $\text{SiO}_2$  barrier being  $127 \pm 30 \mu\text{m}$  by a sol-gel method.

## 1 Introduction

Polyacrylonitrile (PAN) carbon fibers are of a great interest due to their wide application in composite materials, which are used as structural materials in aviation and aerospace engineering. The surface properties of carbon fibers have a great impact on composite materials. To improve the interaction at the matrix/fiber or fiber/coating interface, the surface of carbon fibers is modified [1, 2].

There are two types of surface modification: physical and chemical. Physically, adhesion improvement occurs because of increased roughness; it results in the increased surface area and a large number of contact points, micropores, or surface pits on the already porous surface of carbon fibers. The chemical method includes chemical reactions for the activation of reactive groups contributing to the improved matrix adhesion [3].

Oxidation in acid solutions is one of the simplest and most widely applied methods of fiber surface treatment to improve adhesion; it facilitates an increase in the polymer composite strength. Papers [4–7] describe the modification of carbon fibers in nitric acid during various periods of time. It was shown that the increase in the oxidation degree results in the growth of the oxygen and nitrogen content on the surface. Brunauer-Emmett-Teller (BET) methods confirmed that the total specific surface area increases. An increase of the total surface due to the occurrence of active groups ( $-\text{O}-\text{C}-$ ,  $\text{C}=\text{O}$ ,  $-\text{O}-\text{C}=\text{O}$ ) contributed to a better fiber-polymer matrix adhesion. The results of X-ray photoelectron spectroscopy (XPS) in papers [8–10] showed that oxidation not only affects the oxygen concentration, but also results in observable changes of the nature of chemical functions due to the conversion

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\* Corresponding author: rida\_gallyamova@mail.ru

of hydroxyl-type oxygen into carboxyl one. This process was followed by a decrease in carbon concentration and an increase in oxygen concentration due to surface oxidation.

The crucial factors at the acid treatment of the fiber surface are the concentration of the oxidizing environment, the treatment time and temperature as well as the surface properties of the carbon fibers.

This research studies the impact of the parameters of the carbon fiber acid treatment on the surface morphology and the formation of the C=O, –O–C=O reactive groups.

## 2 Experiments

Carbon fibers obtained from the PAN precursor were subjected to heat treatment at the temperature of 400°C for 20 minutes to remove the sizing from the surface.

To form reactive groups on the carbon fibers' surface, the surface was treated by the exposure of fibers to nitric acid and the acid mix (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>). The authors studied such parameters as temperature, concentration of nitric and sulfuric acids, and the exposure time of the fibers. Annealed carbon fibers 6-8 cm long are immersed into a flask to modify the surface. The flask was filled with 30 ml of concentrated nitric acid, an aqueous solution of nitric acid or acid mix. The water bath was heated to a pre-set temperature. The solution temperature was controlled with a thermometer. The fibers were kept for a certain time and removed from the solution. They were washed in distilled water several times until the pH of the water equaled 7. Further, the fibers were dried in a drying chamber at a temperature of 85°C for 20 minutes. In these research, the initial 65.6% concentration of nitric acid was equated to 100% concentration.

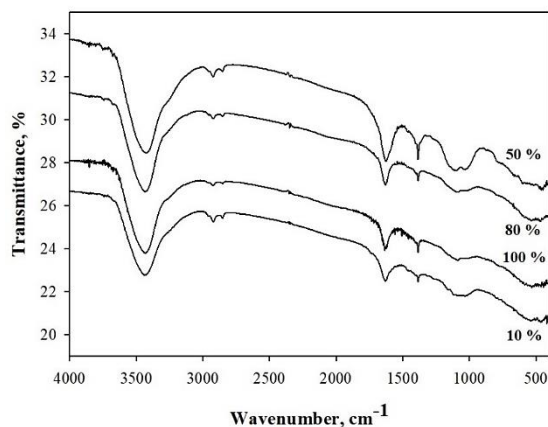
Coatings were applied on the surface of carbon fibers by means of the sol–gel method; the composition of the sol and the deposition technique are described in detail in paper [11].

The surface morphology of carbon fibers was studied with a scanning electron microscope (SEM) Hitachi Regulus SU8220 in the secondary electron mode with an accelerating voltage of 2 kV. The reactive groups on the surface of carbon fibers were assessed with an IR spectrometer Shimadzu IRPrestige-21. IR spectra from the fiber surface were registered in the range of 400-4000 cm<sup>-1</sup>.

## 3 Results

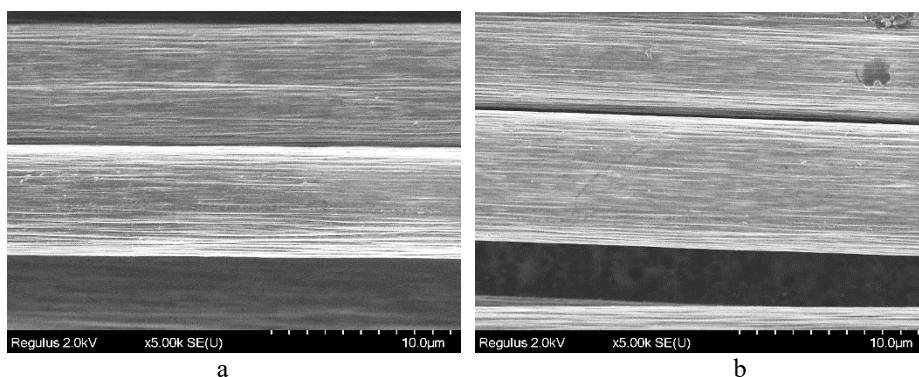
### 3.1 Impact of nitric acid concentration

Fig. 1 shows the IR spectra of the carbon fiber treated at various concentrations of nitric acid. After the oxidative modification of the carbon fiber surface with concentrated nitric acid the absorption bands were observed in the IR spectrum at the regions of 1663-1798 and 1568 cm<sup>-1</sup> corresponding to the bond vibrations of the ketone (C=O) and carboxyl groups (–COOH). The occurrence of carboxyl groups is confirmed by a wide band in the region of 3000–3600 cm<sup>-1</sup> which relates to the vibrations of the –O–H hydroxyl section. The intensity of the absorption bands increases as the concentration of nitric acid increases up to 50%. Intense absorption bands at 1455-1460 cm<sup>-1</sup> refer to C-H vibrations. One may observe the absorption bands of the ketone group at 1633-1700 cm<sup>-1</sup> and the occurrence of the nitrate group peaks (NO<sub>3</sub><sup>-</sup>) at 1380 cm<sup>-1</sup>.



**Fig. 1.** IR spectra of carbon fibers after modification at different nitric acid concentration.

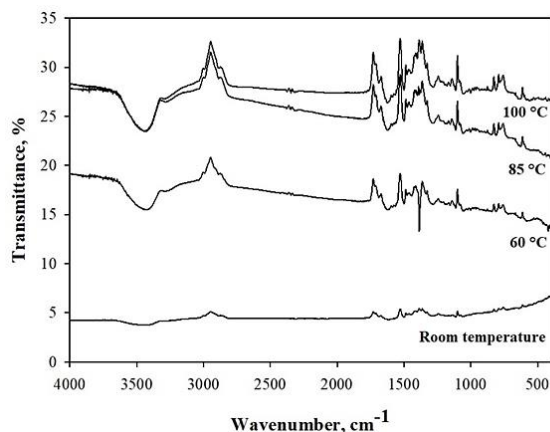
Fig. 2 (a, b) shows SEM images of the carbon fiber surface treated at 10% and 80% nitric acid concentration. After being treated in the 10% nitric acid solution the fiber surface is smoother. An increase in the concentration of nitric acid facilitates an increase in the fiber surface roughness. To evaluate other modification parameters in further experiments, the fibers were treated with 100% nitric acid.



**Fig. 2.** Surface of carbon fiber after acid modification: a) 10%; b) 80%.

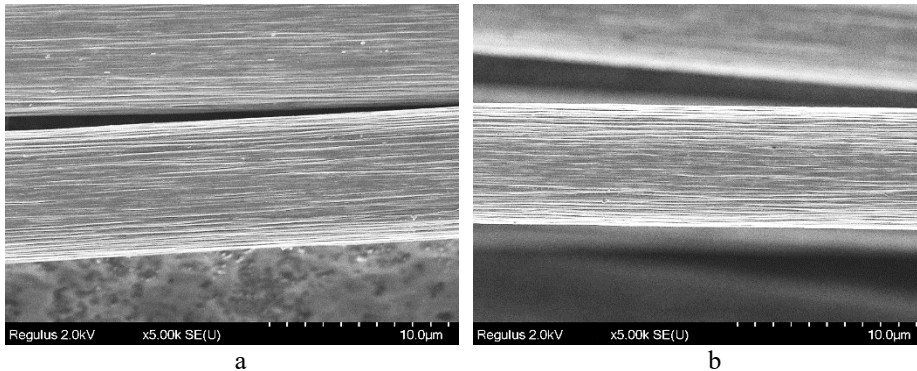
### 3.2 Treatment temperature impact

Fig. 3 shows the IR spectra of carbon fiber at various treatment temperatures with 100% nitric acid. Similar absorption bands in the IR spectrum are observed in the regions of 1663-1798 and 1568  $\text{cm}^{-1}$  which relate to the bond vibrations of the ketone and carboxyl groups ( $-\text{COOH}$ ). Low-intensity bands are observed in the IR spectrum at the ambient temperature in the range of wave numbers 400-4000  $\text{cm}^{-1}$ . A gradual increase in the fiber treatment temperature facilitates an increase in the band intensity within the IR spectrum. Absorption bands are observed in the range of wave numbers of 3000-3600  $\text{cm}^{-1}$  related to the  $-\text{O}-\text{H}$  vibrations while the band intensity of increases significantly with the growth of temperature up to 85  $^{\circ}\text{C}$ . The peaks at 1103 and 1078  $\text{cm}^{-1}$  correspond to the  $-\text{C}-\text{O}-\text{C}-$  bonds. The nitric acid treatment of fibers results in the addition of  $\text{NO}_3^-$  ions which is clear from the occurrence of an intense band in the region of 1375  $\text{cm}^{-1}$ .



**Fig. 3.** IR spectra of carbon fibers after the modification at different temperatures.

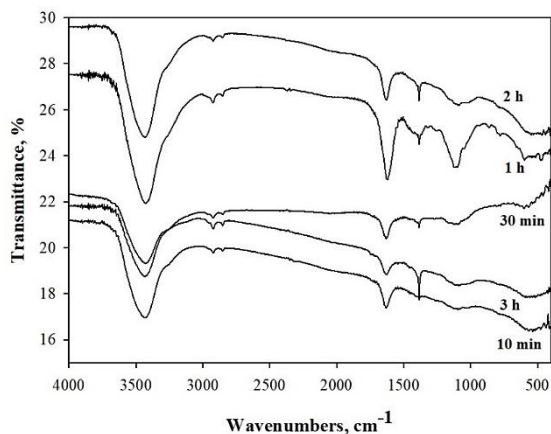
The fibers' surface after acid treatment at the ambient temperature and at 100°C is shown in fig. 4. On the surface of the modified fibers longitudinal bands are observed along the fiber axis. The surface of untreated fibers and the surface of modified fibers at the ambient temperature are almost the same. Temperature increase slightly changes the fiber surface relief. After oxidation one observes the deepening of the longitudinal grooves on the fiber surface.



**Fig. 4.** The carbon fiber surface after acid modification: a) at the ambient temperature, b) at 100 °C.

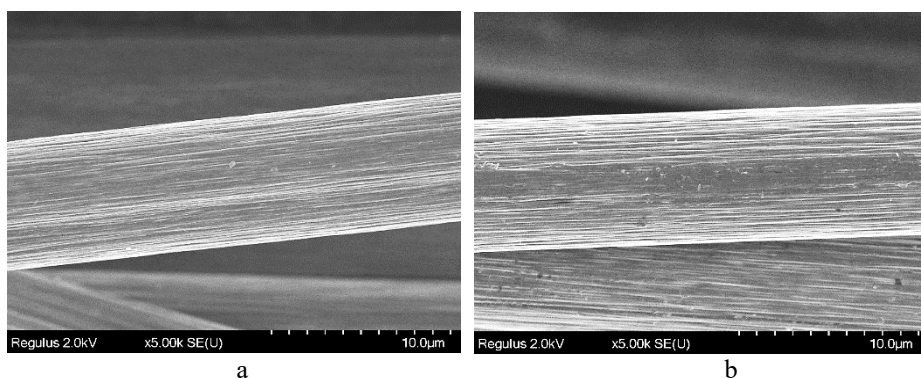
### 3.3 Treatment time impact

IR spectra changes of modified carbon fibers at different treatment periods are shown in fig. 5. The spectra have similar absorption bands as described in the paragraphs above. With a treatment time increase the intensity of the absorption bands also increases reaching a maximum at the 2-hour treatment. Three-hour treatment decreases the band intensity in the IR spectra.



**Fig. 5.** IR spectra of carbon fibers after acid treatment at different exposure periods.

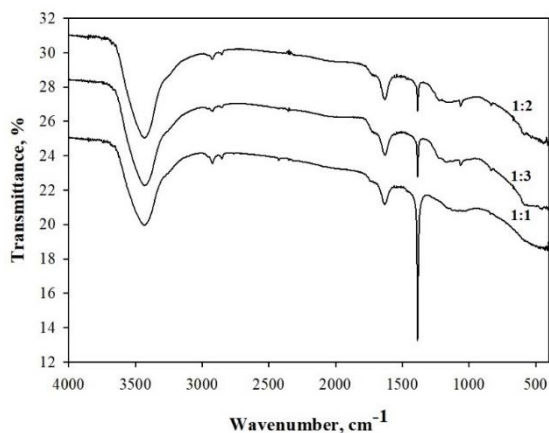
Fig. 6 shows the morphology of the fiber surface at different exposure periods. At the minimum treatment time, the fiber surface is smooth. The 2-hour acid exposure of carbon fibers results in a deepening of the grooves existing and the increased relief of the carbon fiber surface.



**Fig. 6.** The carbon fiber surface after modification: a) at the 10-min exposure; b) 2 hours.

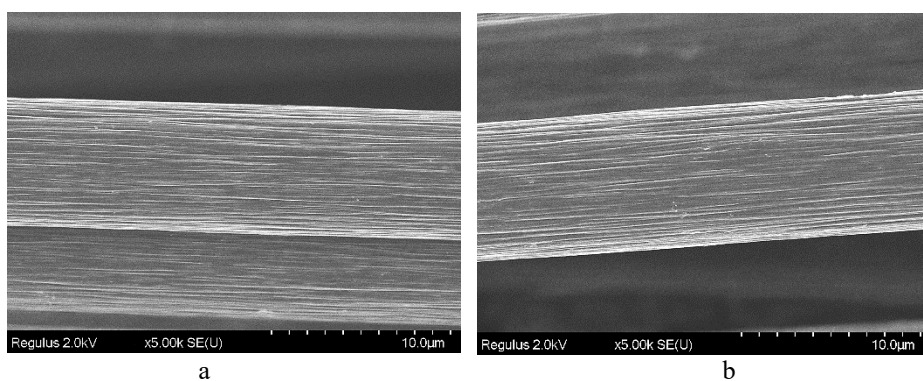
### 3.4 Impact of $\text{HNO}_3/\text{H}_2\text{SO}_4$ ratio

Carbon fiber treatment at various ratios of the nitrosulphuric acid is shown in fig. 7. The region in the range of wave numbers  $3000\text{--}3600\text{ cm}^{-1}$  refers to the vibrations of the  $\text{--O--H}$  hydroxyl section. At a ratio of acids 1:1, an intense peak occurs in the region of  $1375\text{--}1380\text{ cm}^{-1}$ , related to the vibrations of the nitrate group ( $\text{NO}_3^-$ ); the intensity of the latter decreases with an increase in the sulfuric acid ratio. Absorption bands are observed at  $1598\text{ cm}^{-1}$ . These bands refer to the carboxyl groups. No absorption bands of S-containing groups in the range of  $1150\text{--}1230\text{ cm}^{-1}$  were identified in the IR spectrum.



**Fig. 7.** IR spectra of modified carbon fibers with a mixture of acids.

The carbon fiber surface after treatment with nitrosulphuric acid differs significantly from previous treatments (Fig. 8). At the acid ratio 1:1 one can observe already deepened longitudinal bands and surface roughness on the surface. With an increase in the ratio of nitrosulphuric acid to 1:3, the depth of the longitudinal bands increases forming a wavy surface relief. Such impact of nitrosulphuric acid can adversely affect the carbon fiber properties.



**Fig. 8.** The modified carbon fiber surface with a nitrosulphuric acid: a) ratio of acids 1:1; b) ratio of acids 1:3.

## 4 Discussion

The studies conducted show that the concentration of nitric acid significantly affects the intensity of the bands in the IR spectrum. At 10% acid concentration low-intensity absorption bands are observed in the IR spectrum. The maximum absorption is achieved at the acid concentration of 50%, which indicates an increased number of carboxyl, ketone reactive groups. Further increase in acid concentration facilitates the decrease of absorption band intensity. The decrease in the band intensity within the spectra is presumably associated with a decrease in the carbon concentration on the surface which may indicate the destruction of the fiber surface.

Fiber modification at the ambient temperature shows low-intensity bands in the absorption spectra of carboxyl and carbonyl groups. The increase in the treatment temperature to 100°C facilitates an increase in the concentration and intensity of the absorption bands of reactive groups on the fiber surface. The modification within the temperature range of 80-100°C demonstrates a high concentration of reactive groups on the carbon fiber surface.

Varying the processing time of the fibers revealed that, on the one hand, 10-minute treatment is insufficient for the formation of reactive groups on the fiber surface. On the other hand, a longer fiber treatment for 3 hours results in the decrease of the main band intensity in the spectrum, except for the absorption bands of the valence vibrations in the aromatic ring at 1450–1500  $\text{cm}^{-1}$ . Thus, it is recommended to treat the surface of the fibers for 2 hours as a longer treatment may cause excessive oxidation of the fiber surface, which, in its turn, will deteriorate its properties.

Similar absorption bands are observed in the IR spectra of the nitrosulphuric acid as those observed at other parameters of the fiber surface modification. An increase in the intensity of absorption bands is observed in the range of wave numbers 1450-1500  $\text{cm}^{-1}$ . Moreover, the intensity of these bands decreases with the increase in the sulfuric acid content. Sulfur-containing reactive groups were not detected in the spectra.

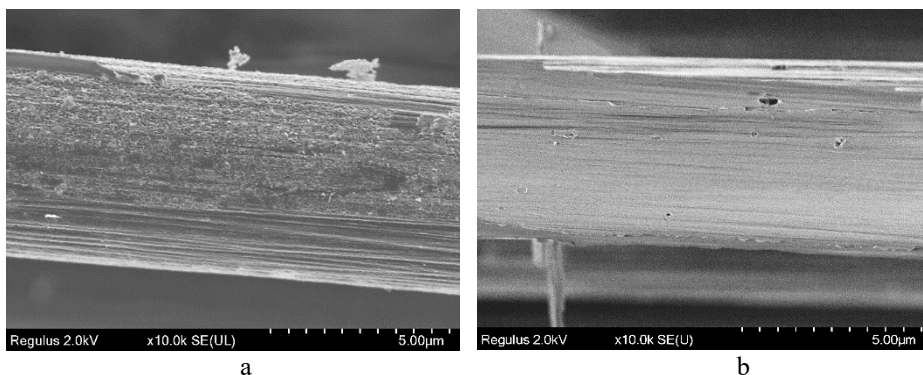
It should be noted that the higher the temperature, time, and concentration of the solution are, the higher the degree of surface oxidation is; the latter factor results in the decreased number of reactive groups formed on the fiber surface (according to IR spectra).

Acid treatment of the fiber surface results in a significant relief deepening (longitudinal groove deepening) on the surface (Fig. 8b). The relief becomes more marked with the increased temperature, time and solution concentration.

To assess the acid treatment effect on the formation of oxide barrier coatings, silicon oxide was applied on the surface of carbon fibers by the sol-gel method. The coatings were applied by immersion into a sol-gel solution with an exposure time of 15 sec and slow removal from the solution. Next, the coated fibers were subject to heat treatment in order to form the  $\text{SiO}_2$  coating. The coating was applied to the original fiber without preliminary surface acid modification and after the modification in concentrated nitric acid (100 °C, 2 h).

The carbon fibers after coating application are shown in fig. 9. The coating on the fibers without surface modification was formed unevenly; one can observe the areas having flaws in the form of chips and delaminations (Fig. 9a). The coating thickness is  $190 \pm 58$  nm.

The fiber surface modification results in the formation of a uniform, homogeneous  $\text{SiO}_2$  coating of  $127 \pm 30$   $\mu\text{m}$  (Fig. 9b). The fiber surface has virtually no coating flaws.



**Fig. 9.** Coated fiber surface: a) before acid modification of the surface; b) after acid modification.

## 5 Conclusion

The authors found out the presence of carboxylic and ketone reactive groups in the range of 1663-1798 and 1568  $\text{cm}^{-1}$  within the IR spectra of carbon fibers. The use of a nitrosulphuric acid did not reveal S-containing reactive groups in the IR spectra of carbon fibers. An increase in temperature, time, and concentration of acids leads to a decrease in the intensity of absorption bands in the IR spectrum corresponding to carboxyl and ketone reactive groups.

The preliminary acid treatment of carbon fibers facilitates the formation of a uniform and homogeneous  $\text{SiO}_2$  coating during its application by the sol-gel method. The thickness of the  $\text{SiO}_2$  coating after oven drying is  $127 \pm 30 \mu\text{m}$ .

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