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Microwave induced hierarchical nanostructures on aramid fibers and their influence on adhesion properties in rubber matrix

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Abstract

At the moment several commercial surface treatments are used to increase adhesion between aramid fiber and matrix material in composite structures but each of these have some limitations. The aim of this study is to address some of these limitations by developing a surface treatment method for aramid fibers that would not affect mechanical properties of the fibers negatively, could be used with any matrix material and that could withstand handling of the fibers and ageing. The method used is microwave assisted surface treatment that uses microwave radiation together with dry reactive chemicals to create hierarchical structures to the fiber surface and so makes it possible to control the adhesion properties of the fibers. SEM imaging, fiber tensile tests and modified bundle pull-out test were used to investigate the outcome of the surface treatment and measure adhesion between aramid fiber bundles and rubber. SEM imaging revealed that nanoscale deposits are formed on to the fiber surface which enable mechanical interlocking between the fiber and the matrix material. Fiber tensile tests showed that the surface treatment does not influence tensile properties of the fiber negatively. Results from the bundle pull-out tests confirmed that this kind of method can lead up to 259% improvement in adhesion when compared to untreated aramid fibers in rubber matrix.

Keywords: aramid fiber, surface modification, microwave treatment, mechanical interlocking, adhesion, hierarchical structures

1. Introduction

Aramid fibers are high strength and high modulus synthetic fibers that are typically used in demanding composite applications, such as tires and hoses, where a strong interfacial bond between reinforcing fiber and matrix material is needed but also in applications where the controllability of the interfacial adhesion is important, such as bullet proof vests [1]. However, the adhesion properties of aramid fibers are difficult to control and thus, the whole potential of the fiber is not yet utilized at the moment. The chemical structure of aramid fiber is such that there are aromatic rings and amine bonds linked to the polymer backbone that induce high crystallinity and rigidity [2], [3]. The fiber surface is very smooth and chemically inert, lacking functional groups on the fiber surface [2], [4]. Thus, it is difficult to achieve good adhesion with the matrix material as it cannot form strong covalent bonds with the matrix. Poor adhesion at the fiber-matrix interface greatly limits the structural performance of whole composite structure.

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Methods to increase adhesion of aramid fibers have been studied widely and they continue to be a topic of great interest in the industrial and academic world. Currently used methods often aim to change the chemical structure of the fiber surface [5], [6], [7] or to add a substantial coating to the fiber surface [8], [9] that enables bonding with the matrix material. However, the problem with these methods is that they are specific to certain matrix material only [8], the effect of the treatment wears off with time [5] or they lower the tensile strength of the fiber [10]. Thus, a matrix material independent, stable and a non-damaging method for the surface treatment is highly desirable.

An approach to overcome the matrix dependency would be to introduce hierarchical structures [11] to the fiber surface that would enable mechanical interlocking between fiber and matrix rather than chemical bonding. Very promising results have been achieved with this kind of research with hierarchical structures on carbon fibers [12] and also with aramid fibers [13], [14], [15]. In an earlier study [14] functionalized multiwalled carbon nanotubes were successfully grafted to Kevlar by immersion, which increased interlaminar shear strength of Kevlar-epoxy composites by 30%, compared to untreated fibers. Similar results [15] were achieved with a hybrid coating of SiO_2 and shape memory polyurethane. With this kind of coating interfacial shear strength of aramid fibers increased by 45% compared to uncoated fibers. In a more recent study [13] zinc oxide nanowires were grown on to aramid fabric in a hydrothermal growth solution. Also with this method a significant increase in interyarn friction could be achieved, when compared to untreated fabric. All of these methods, however, require several steps, wide variety of chemicals and long treatment times. From an industrial point of view it would be beneficial to develop a simpler method. In this study hierarchical structures are introduced to aramid fiber surface by the means of microwave radiation in a rapid and rather simple two-step procedure using microwave radiation that also allows to control the adhesion properties of the fibers.

Microwaves have been used in several industrial processes from catalyst preparation [16] to mineral treatment [17] because they enable direct and internal heating. Also in a quite recent study [18] microwaves were used to manufacture carbon nanotubes in the presence of graphite and ferrocene bis(η5-cyclopentadienyl)iron. This method was successfully used to treat woven aramid fibers in a study by Hazarika et al [19]. They were able to grow iron particle decorated carbon nanotubes to activated woven Kevlar fibers. The basis of the process was following: when graphite is subjected to microwave radiation, it heats up rapidly and transfers the heat to ferrocene, which then decomposes to atomic iron. Atomic iron condenses and aggregates into iron nanoparticles into which carbon atoms diffuse. When the saturation point of the nanoparticles is reached, the growth of carbon nanotubes begins. With their method Hazarika et al. were able to increase the in-plane shear strength of aramid-polyester resin composites by ~81% [19]. However, they did not investigate the effect of the surface treatment to the tensile strength of the individual fiber filaments.

In this study, ferrocene and graphite are used as reactive chemicals to modify aramid fiber surface with microwave radiation to control adhesion properties. The surface treatment process is faster and more simple than the ones used in previous studies. Also, as the chemicals are not in physical contact with the fibers, it may make the process more easily adapted for continuous industrial processing, than some of the other methods. The effect of the surface treatment is studied visually with scanning electron microscopy (SEM), atomic force microscopy (AFM) and optical microscopy as well as physically with fiber tensile tests and modified bundle pull-out tests to composite structures.

2. Materials

Aramid fibers used in this study were para-aramid yarn Twaron 2201 (tensile strength 2.1 N/tex, linear density 1610 dtex, 1000 filaments in a fiber bundle) with ~0.15 w-% of water soluble surface sizing with EO and PO alcohol components, as stated by manufacturer. The surface sizing is used with aramid to make the fibers antistatic to help with processing and handling. To investigate the effect of the surface sizing added during the

manufacturing process of the fibers, some samples were washed with mild detergent, rinsed with ethanol and dried in vacuum for 12 h before surface treatment. These fibers are referred to as "pre-washed" fibers. Other fiber samples were treated in their as-received state. It is already known [7] that a small amount of oil used in surface sizing does not influence the outcome of some adhesion promotion methods negatively but rather improves the outcome by creating more even finish. Thus, it is interesting to know how the surface sizing effects the outcome of this surface treatment process.

Reactive chemicals used in the microwave treatment process were ferrocene (98%, Aldrich Chemistry) and graphite (Timrex KS44, Timcal Switzerland) in powder form. In the surface treatment process graphite acts as a support material for ferrocene because graphite absorbs microwave radiation readily and also helps to transfer the heat, created by the radiation, to ferrocene. This way a rapid chemical reaction is created.

Rubber, used for the making of the composite pieces for adhesion testing, was butadiene based rubber provided by Nokian Tyres. Rubber was chosen as matrix material because aramid fibers are widely used in rubber composites but it is not very much used matrix in adhesion studies. Also, the traditional recorcinol formaldehyde latex (RFL) treatment for aramid fibers in rubber matrix uses formaldehyde, which is considered to be carcinogenic and harmful [23]. Thus, it is beneficial to investigate if the surface treatment presented in this study, would be compatible with rubber as well.

3. Methods

3.1 Surface treatment process

Surface treatment method in this study uses microwave energy to induce nanoscale deposits onto aramid fiber surface. Often aramid fiber surface is pre-treated prior to any further surface treatment to activate the surface [15]. In this study Agar Turbo carbon evaporator B7230 (Agar Scientific, United Kingdom) was used to deposit a thin layer of carbon on to the fiber surface before the actual microwave treatment. The thin carbon layer made the fiber surface more reactive to the heat accumulation [25] during microwave irradiation [26], [30]. During the deposition process the amount of deposited carbon was visually monitored and an optical color reference was used to indicate optimum amount of carbon. To identify the optimum color reference, the effect of carbon amount was first investigated. It was noticed that too low amount creates only a slight coverage of nanodeposits on the fiber surface. The aramid fibers were carburised as fiber bundles. The fibre bundles were overturned during the carburizing process to enable carbon to adhere on all sides of th bundle. This way more even coverage with carbon was achieved. However, it was anticipated that the fibers inside the fiber bundle will not be as completely covered with carbon as the ones on the outlayers of the bundle.

For the surface treatment process 1:1 ferrocene and graphite, in powder form, were placed to the bottom of a glass container and carburized aramid fibers were added, in a way that they were not in physical contact with the chemicals, as presented in Figure 1. The glass container was sealed with a plastic cap to create a constant gas atmosphere for the chemical reactions to take place. In this case the constant gas atmosphere means that no vapors produced by the reaction are able to escape the container during the radiation process.
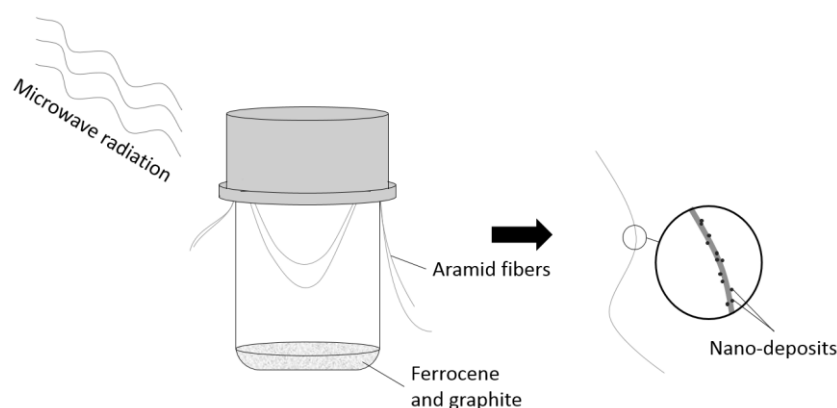
Fig. 1. Schematic drawing of the microwave assisted surface treatment process.

The glass container holding the fibers and the chemicals was placed into a microwave and exposed to microwave radiation for set time at full power. The source of the microwaves used, was a commercial microwave oven (UPO M1770 with 230V, 50Hz and 1150W). The exposure time to microwaves was varied to investigate its effect on the outcome of the surface treatment. Sample sets with 6, 10 and 14 seconds exposure time were made. Shorter and longer exposure times were also tried; less than 5 seconds did not give enough time for the initial high-energy reaction to take place and no bright white flash indicating the reaction between ferrocene and graphite could be seen. On the other hand, irradiation times longer than 15 seconds initiated no ultimate difference in properties or appearance of the fibers after the procedure. Even longer radiation times caused scorching of the fibers. After the microwave radiation the samples were removed from the container, rinsed with ethanol, to remove soot caused by the treatment, and let dry in ambient conditions. The dried samples were blasted with pressurized air to remove any loose particles from the fiber surface.

3.2 Microscopy

To verify the success of the surface treatment, the samples were characterized with scanning electron microscope (SEM) Zeiss ULTRAplus (Zeiss, Germany). For imaging the fibers were attached to aluminum sample holders with carbon glue and carburized to improve conductivity. Atomic force microscopy (AFM) Veeco MultiMode NanoScope (Veeco, USA) was used to examine the fiber surface in more detail. For this, fiber samples were fastened to a glass slide with double-sided adhesive and the glass slide fixed to a circular magnetic sample holder with superglue. Tips used were $0.01 - 0.025$ Ohm-cm Antimony (n) doped Si with reflective Al –coating on the backside (Bruker, model: NTESPA). The acquired AFM images were processed and analyzed with Gwyddion [31] software. A stereomicroscope Leica MZ7.5 (Leica Microsystems, Germany) was used to study the aramid fiber bundles after the bundle pull-out test.

3.3 Fiber tensile testing

To investigate how the treatment affects the tensile properties of the fibers, a fiber tensile tests to single fiber filaments were performed. The test was performed with a Favigraph fiber tensile tester (Textechno Herbert Stein, Germany) according to the ISO 5079:1995. Surface treated samples, samples microwave irradiated without chemicals and samples that were in as-received state (referred to as untreated fibers) were tested. The test was performed in a controlled environment (20 °C ±2 °C, 65% RH ± 4% RH) according to the ISO 139:2005.

3.4 Manufacturing of aramid-rubber composite

After the surface treatment the fibers were cast in butadiene based rubber and vulcanized to create composite pieces for adhesion testing. Steel molds were used for the casting as presented in Figure 2a. The dimensions of the mold were such that in each case 2 cm of fiber length was embedded in the rubber. The samples were vulcanized (160 °C, 12 min) in a press according to parameters determined by a cure test done with Advanced Polymer Analyzer APA2000 (Alpha Technologies, USA). A complete vulcanized composite sample in the mold is presented in Figure 2b. Aramid fibers protruding through the mold were tied together to prevent tangling.
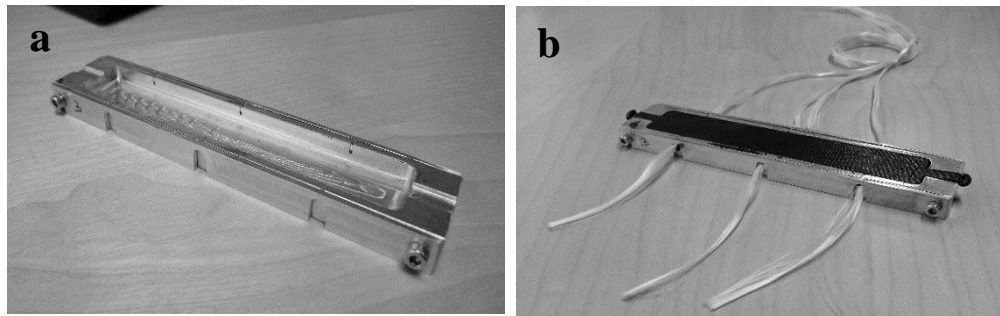

Fig. 2. a) Aluminum mold for rubber casting and b) vulcanized aramid/rubber composite piece.

3.5 Adhesion testing

A modified bundle pull-out test was used to investigate the effect of the surface treatment on adhesion properties. In this bundle pull-out test whole fiber bundles were extracted from rubber matrix. This type of method correlates better with the actual use and behavior of aramid fiber composites than the often used single fiber pull-out test [20]. For the adhesion testing the cast sample was cut into three, approximately identical, pieces. The longer end of the fiber was tied to a metal piece for the tensile tester's upper jaw to grab on to. This is done to minimize the effect of lateral compression on the results. A sample ready for the adhesion testing with tensile tester is presented in Figure 3.
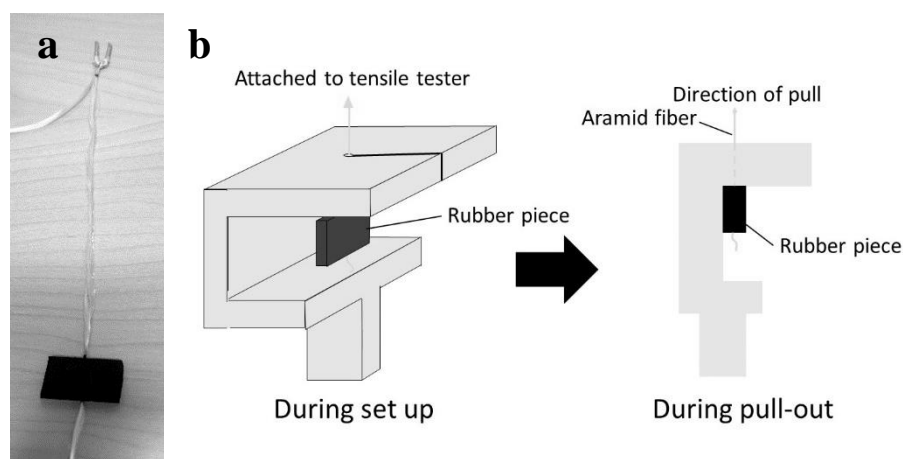

Fig. 3. a) Sample for adhesion testing, b) position of the sample in the specimen holder during set up and a cross-sectional view during pull-out.

For the adhesion testing the sample was placed into the tensile tester. The specimen holder used (Fig. 3b) did not clamp the sample in any way. This type of sample holder provided a clear benefit over some of the most used methods for adhesion testing in rubber, such as H and U-adhesion tests. In these tests tensile tester grips the rubber sections of the test samples which may cause uneven stress distributions within the sample and

affect results [27], [28]. The modified bundle pull-out test was performed with a Instron 5967 tensile tester with 2 kN load cell. The test was initiated with a pretension of 1 N to ensure smooth and repeatable pull for each of the samples. Pull-out speed was 5 mm/min. Load and displacement are recorded during the test. After pull-out the fibers were studied with stereomicroscope to investigate the condition of the fiber bundle and the amount of rubber residue that has adhered to the fiber bundle.

4. Results and Discussion

4.1 Scanning electron microscopy

The effect of surface activation of the aramid fibers with carbon was investigated with SEM and the results are shown in Figure 4. It is clear that the surface activation with carbon enhances the effect of the surface treatment significantly and a more robust and even coverage could be achieved. This is because carbon absorbs microwave radiation readily creating heat [18]. Localised heat build-up at the fiber surface lovers the activation energy barrier of the reaction creating the nanoscale deposits on the fiber surface. However, due to the heat build-up, excess carbon on the fiber surface may cause damage and in most severe cases burning of the fibers.
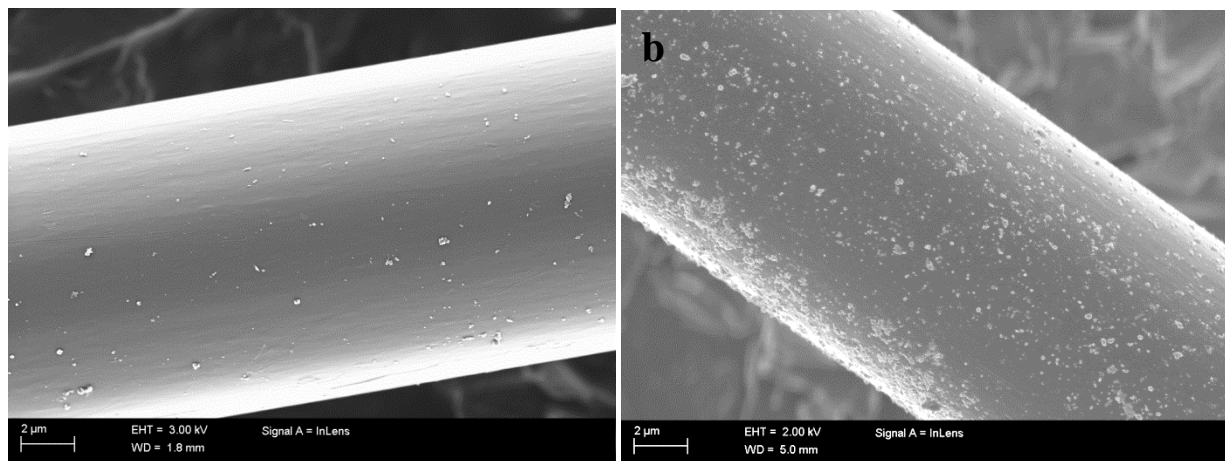

Fig. 4. Aramid fiber after microwave surface treatment with irradiation time of 14 seconds: a) without surface activation, b) with surface activation with carbon prior to surface treatment.

SEM was also used to study the surface structure of the aramid fibers after the surface treatment, the results are presented in Figure 5. The images show small nanoscale deposits that have formed on the fiber surface. It can be seen that there is a clear difference in deposit size and coverage of the fiber surface area depending on the treatment time used. An image analysis (Table 1) was conducted to determine the percentage of surface area covered by the deposits and the mean particle size of the deposits with each treatment time. The mean particle size was calculated as an arithmetic mean.
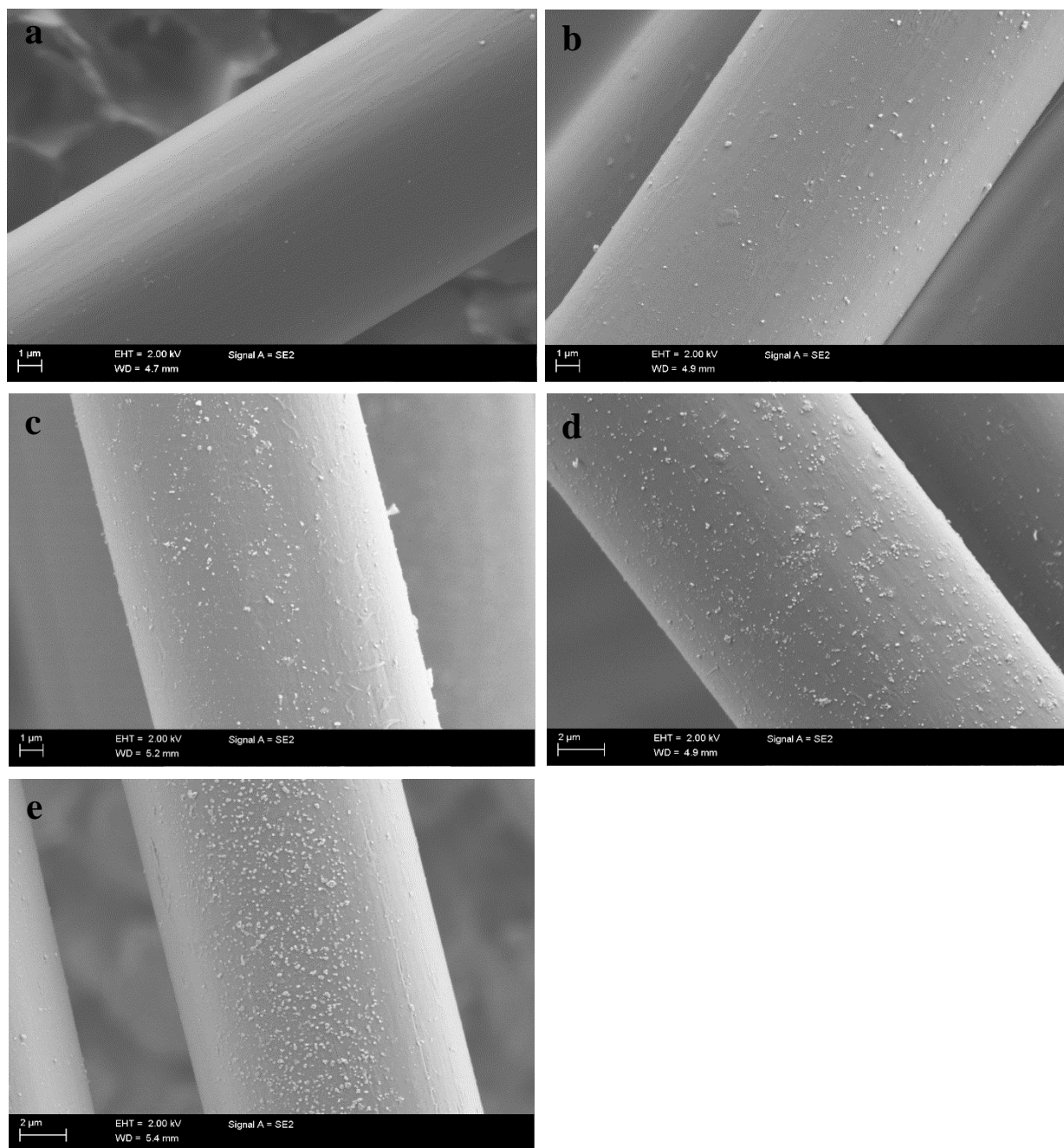
Fig. 5. SEM images of aramid fiber filaments with a) being a control sample and b) a surface treated sample with the irradiation time of 6 seconds, c) 10 seconds, d) 14 seconds and e) 14 seconds with a prewashed fiber.

Table 1. Results of image analysis of SEM -images of the nanoparticles on the surface treated samples. Area analyzed in each case was at minimum an area of 5 x 8 µm.

Sample	Count	Mean particle size [μm^2]	Surface area coverage [%]
6s	145	0.008 (±0.0089)	2.1
10s	379	0.008 (±0.0120)	4.7
14s	449	0.008 (±0.0116)	7.2
14s (prewash)	681	0.013 (±0.0157)	16.0

The analysis revealed that by increasing the treatment time the number of nano-deposits increased. Thus, by increasing the treatment time, the area of fiber surface covered by the nano-deposits increased. From the SEM images and the image analysis became clear that the formation of nano-deposits on to the fiber surface is a rapid process and even with 6s radiation time deposits were formed. This indicates that by controlling the irradiation time, the surface structure can also be controlled. However, much longer irradiation times are not practical as the outcome hardly changes.

When analyzing the results for the prewashed fibers (Figure 5.e), it can be seen that the amount and mean particle size of the deposits increased significantly when compared to the other fiber samples (Figure 5.b-d). This also had an effect on the surface coverage, which had roughly doubled. The fibers used in this study were of low manufacturing related surface sizing content (~0.15 w-%), so pre-washing of the fibers was not anticipated to have a great effect on results, as de Lange and his colleagues had previously [7] noticed. However, at least in this case removing the surface sizing from the fiber proved to be beneficial to the success of the surface treatment. This phenomenon may be due to a secondary aspect caused by the removal of the surface sizing and its effect on static electricity. It may be, that the slightly charged prewashed aramid fibers may have attracted the carbon particles more during carburizing process to the fiber surface, thus creating a more even coverage with carbon. Another explanation may be the polar nature of aramid fiber surface. It is known that the polar surface of aramid fibers attracts water molecules, which can disrupt the molecular arrangement on the fiber surface by bonding with the hydrogen bonds interconnecting the main polymer chains [21], [29]. As the prewashing step was a water based procedure, hydrogen bonds on the fiber surface may have re-organized themselves and the new arrangement became more favorable for the carburizing process.

When taking a closer look at the nanodeposits (Figure 6), it seems that they are bonded to the fiber surface rather than just resting on the surface. This indicates that the deposits are securely attached to the surface and should have an effect on adhesion properties of the fibers. This also shows, that the pressurised air used, after the surface treatment process, has removed most of the loose particles from the fiber surface. Only the ones that are firmly attached have remained on the fiber surface, which means that the surface treated fibers have good handling properties and they should be able to handle industrial composite product manufacturing processes and storage well.
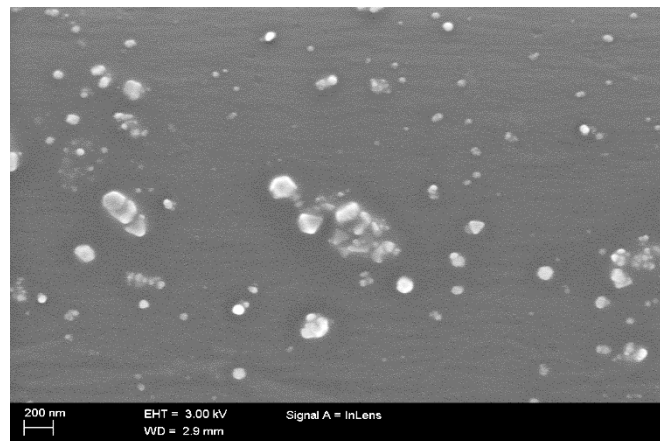

Fig.6. Close-up of nanoscale deposits on aramid fiber surface with SEM.

4.2. Atomic force microscopy

Aramid fibers were examined with AFM to get a more detailed view (Figure 7) of the nanodeposits on the fiber surface and of the fiber surface prior to any surface treatment.
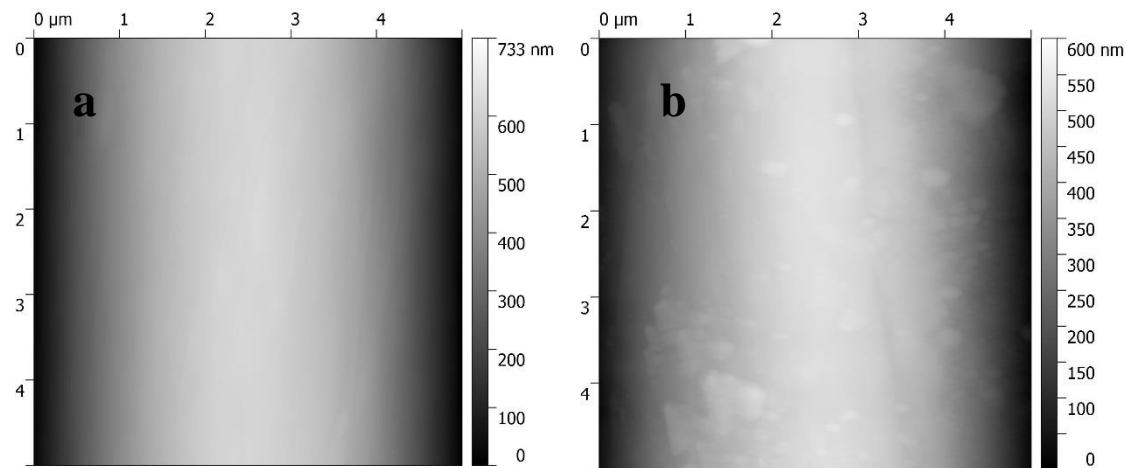
Fig. 7. AFM images (5x5 µm) of a) non-surfacetreated aramid fiber and b) surface treated aramid fiber with microwave irradiation time of 14 seconds.

AFM images reveal the change in surface structure of the fibers due to the microwave assisted surface treatment clearly. Characteristic grooves visible on the untreated fiber (Figure 7a) are caused by the solution spinning process during manufacturing [24]. Nanodeposits, created during the surface treatment process, are clearly visible in Figure 7b. This supports the findings made with SEM in Chapter 4.2. A 2x2 µm size close-up (Figure 8) of the nanostructures shows that the structures have irregular surface topography, as was noted in the image analysis of the SEM images. The presence of these nanostructures with the irregular surface structure together indicate an increase in the surface area of the fibers, which is expected to have an positive effect on the adhesion properties of the fibers.
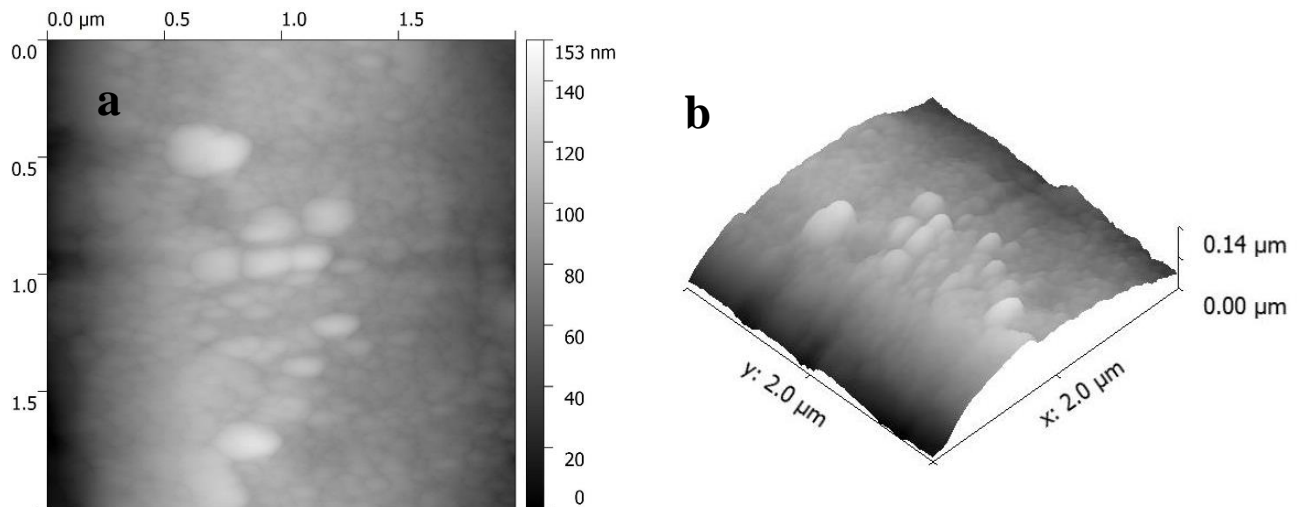

Fig. 8. AFM image (2x2 µm) close-up of a) nanostructures on aramid fiber surface generated during the surface treatment process and b) 3D representation of the same area.

4.3 Fiber tensile tests

Fiber tensile tests were performed to three different samples: surface treated fibers, samples treated with microwaves but without chemicals and untreated fibers. This was done to make sure that this surface treatment process would have no negative effect on tensile properties of the fibers, which is often the case with surface treatments for aramid fibers [10]. The tensile tests were performed to with single fiber filaments. Results of the tensile tests are presented below in Figure 9.
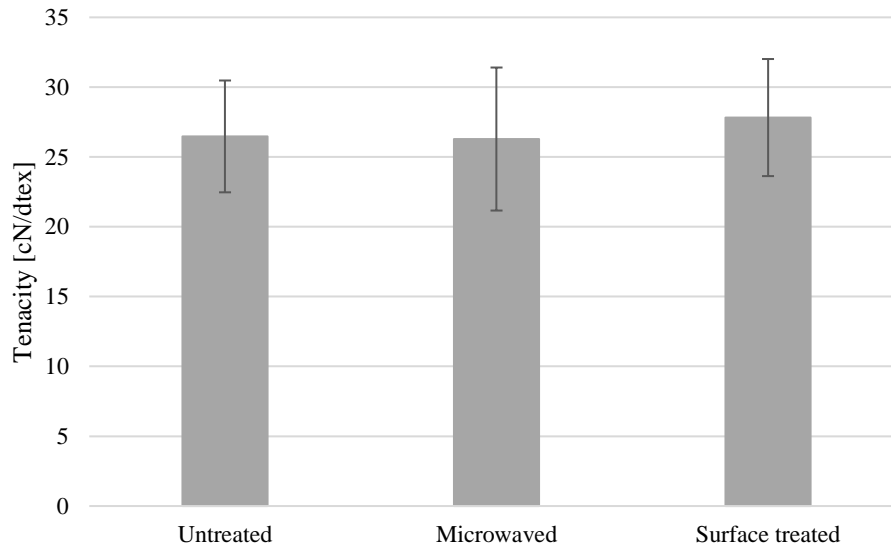
Fig. 9. Results of the single fiber filament tensile tests.

It is known that the elastic properties of aramid fiber vary greatly within the fiber; elastic modulus is significantly higher at the core of the fiber than on the very surface [22]. So the surface layer does not have a very big impact on the overall tensile properties. When looking at the results of the tensile tests, it is clear that no negative impact on the tensile strength has occurred. This was expected, as the reactive chemicals in this surface treatment affect only the very top most surface layer of the fibers. The microwave radiation, on the other hand, will penetrate the whole fiber and affect the bulk material as well but from the results it can be seen that the effect is neither very big nor negative. It looks that the surface treated samples even have slightly increased tensile strength when compared to the untreated samples. It may be that the intense localised heat from the reaction between ferrocene, graphite and carbon has repaired some surface defects in the fibers, like Wenxin [12] found with carbon fibers, resulting in slight increase in tensile strength. However, the increase was so small that no definate conclusions could be drawn from it.

4.4 Adhesion strength

To investigate what effect mold fill has on the adhesion properties an experiment was done where different amounts of rubber were used during casting. The experiment was done with 12.00 g, 12.25 g and 12.50 g of rubber as measured by weight. It revealed that as long as the mold is completely filled during vulcanizing, the amount of rubber does not affect adhesion strength. This was because the excess rubber did not increase the pressure in the mold, which in turn would have enhanced wetting by forcing the molten state rubber in-between the fiber filaments. Instead, excess rubber spilled from the mold through the flow channels during the vulcanizing process. From Figure 10b it can be seen that the aramid fibers are nicely encased in rubber and no significant voids or pores are present. This indicates that the molding process as well as the molds worked well and a reliable test set can be manufactured this way.
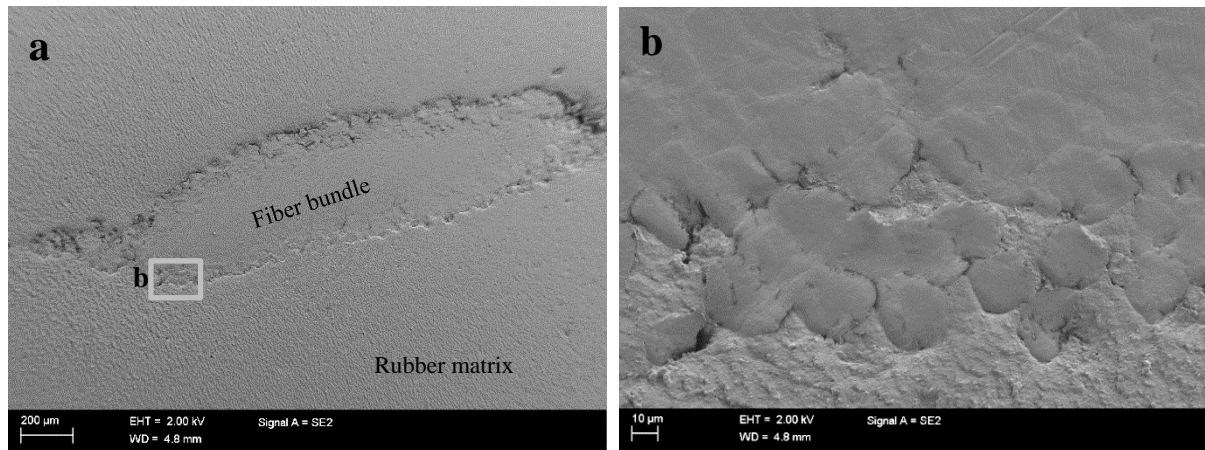
Fig. 10. a) Cross-section of fiber bundle encased in rubber matrix and b) close-up of the fiber-matrix interphase from the location indicated in a).

The results of the modified bundle pull-out test are presented in Figure 11. The microwave assisted surface treatment did indeed increase adhesion, when compared to untreated aramid fibers. The pull-out force increased 102%, 103% and 124% for the samples irradiated for 6, 10 and 14 seconds, respectively, when compared to the untreated fibers. It can also be noted that by removing the manufacturing related surface sizing from the fiber surface prior to surface treatment, an even greater effect can be achieved.
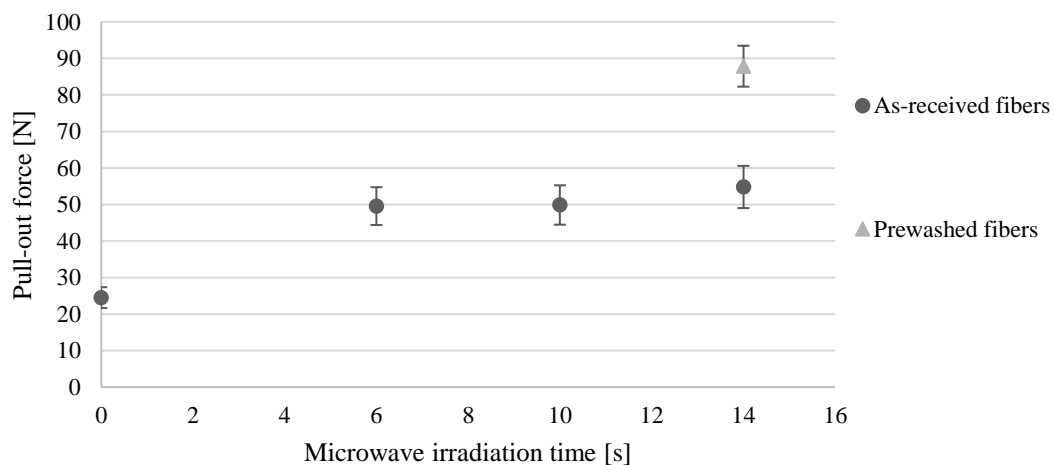

Fig. 11. Interfacial adhesion between rubber and aramid fibers as a function of microwave irradiation time. Data point at 0 seconds refers to untreated reference fibers and the data point nominated by a triangle to the prewashed fibers.

The greatest improvement was achieved with the prewashed samples, where adhesion increased by 259%. However, when the surface sizing was removed from the fibers, static charges could build in the fibers. This may have improved the outcome of the carburizing process as the slightly charged fibers may have attracted carbon atoms more efficiently during the process, creating a more even coverage with carbon. This has increased the amount of nanodeposits on the fiber surface, as stated in chapter 4.1, but it also made handling of the fibers more difficult. The fibers were attracted to other charged surfaces, which made them prone to tangling. These tangles within the fiber bundle can increase mechanical interlocking by creating secondary hierarchical structures to the fiber bundle. These structures in return can influence the adhesion properties of the bundle positively and increase the overall adhesion of the fiber bundle.

When comparing the adhesion test results to the SEM images (Figure 4) and the results from the image analysis, it could clearly be seen that the adhesion between the fibers and rubber matrix had increased

significantly even with the shortest treatment time, which indicates that mechanical interlocking has significantly contributed to the increase in adhesion. With 6 seconds treatment time SEM showed only small nanodeposits sparsely distributed on the fiber surface but adhesion strength, never the less, had doubled. As the surface area, that was covered by the nanodeposits, increased, so did the adhesion to the matrix material, as seen in Figure 12. The effect is almost linear. This indicates that the increase in adhesion strength was not caused just by the possible secondary hierarchical structures caused by fiber tangling, as discussed previously in this chapter. Also, it showed that with this method the adhesion properties of the fibers can be controlled. By increasing the microwave irradiation time the surface area coverage with nanodeposits increased, which lead to an increase in adhesion between the matrix and the fibers.
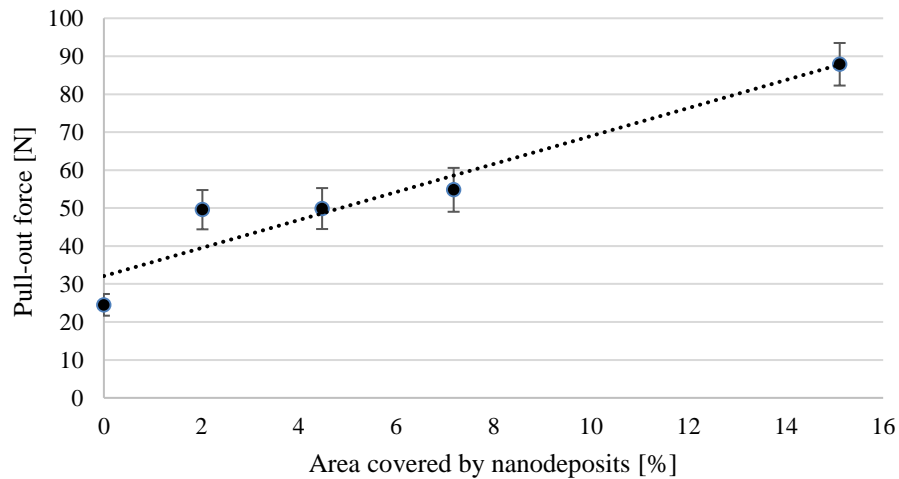

Fig. 12. Pull-out force of the fiber bundles as a function of area on fiber surface that has been covered by the nanodeposits.

Fiber bundles were investigated with stereomicroscope after the pull-out. From the images (Figure 13) it can be seen that failure has occurred mainly along the interface between the fiber and the matrix when looking at the untreated aramid fibers. During pull-out the fibers have slid from the rubber relatively smoothly and only a little rubber residue has been detached from bulk material.
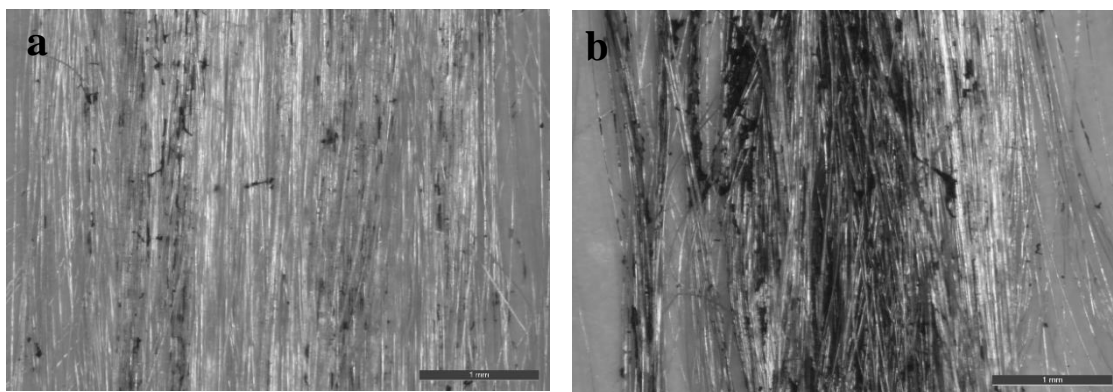

Fig. 13. Stereomicroscope images of aramid fiber bundles a) without any surface treatment and b) with 14s surface treatment after pull-out.

As the "rough" nano-deposit covered fiber bundle was pulled out, the nodules on the fiber surface have ploughed through the rubber tearing bits off and leaving significantly more rubber residue to the fiber bundle. This indicates that the matrix structure has been weaker than the nanostructures on the fiber surface, which further suggests that the nanostructures are very strongly attached to the fiber surface creating a strong and robust network of contact points.

The results, achieved in this study with the microwave assisted surface treatment, are comparable with results of other studies [15], [14], [19] where hierarchical structures are induced to the fiber surface to increase adhesion. In further studies it would be interesting to compare the results of this surface treatment to RFL treated aramid fibers. However, RFL is typically applied only to cord or woven fibers, which have different surface structure to loose fiber bundles, which influences the results. Here the increase in adhesion was achieved with nano-deposits protruding from the fiber surface, mechanical interlocking is the main adhesion mechanism, as also Hazarika et al. stated in their study [19]. Mechanical interlocking is universal to all material types, which suggests that an increase in adhesion may also be achieved with other matrix materials as well. Thus, the introduced method can be utilized in a wide variety of applications.

6. Conclusion

The aim of the study was to find a surface treatment method for aramid fibers which would increase adhesion of the fibers by creating hierarchical structures to the fiber surface and which would not influence the tensile strength of the fibers negatively. Single fiber tensile tests verified that the surface treatment method does not decrease tensile strength of aramid fibers. A modified fiber bundle pull-out test indicated that a 102 - 259% increase in adhesion strength can be gained with this method depending on the test parameters. By varying the microwave irradiation time, the adhesion properties of the aramid fibers can be controlled. However, the best results can be achieved only by activating the surface of the fibers with carbon. This way a more complete coverage of the fiber surface with nano-deposits is possible, which directly influences adhesion strength. The pull-out tests showed that the nano-deposits are tightly attached to the fiber surface and can withstand handling of the fibers without compromising the surface treatment. This indicates that the nano-deposits can most likely also handle long storage times without detaching from the fiber surface. Further studies will be conducted on characterization of the nanodeposits and determination of chemical bonds between the deposits and fiber, as well as on aging of the surface treatment.

Acknowledgements

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