

DIRECT ELECTROPOLYMERIZATION OF POLYMER ELECTROLYTES ONTO CARBON FIBERS – A ROUTE TO STRUCTURAL BATTERIES?

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Abstract

In an effort to further reduce weight of carbon fibre reinforced composites, the concept of structural batteries has arisen. A structural battery is a multifunctional material managing both energy storage and enabling of structural integrity. More specific, the carbon fibres in the composites are used as negative electrode in a Li-ion battery. A crucial part of such a battery is the preparation of a thin, ionically conductive and stiff polymer matrix. One route to realize this is the use of electropolymerization, which can cover each individual fibre with polymer. In this study, the surface morphology of coated carbon fibres is investigated with electron microscopy and atomic force microscopy. Additionally, the curing degree as a function of process temperature during polymerization is tested.

1. Introduction

Carbon fibre reinforced polymers (CFRP) are in general used to create light-weight structures. Introducing CFRP in vehicles, such as in the automotive and aerospace industries, creates lighter vehicles with lower energy consumption, which in turn improves both economic and ecological sustainability [1]. The potential for further weight-loss have opened up over recent years, since a number of hybrid and even fully electric vehicles (EV) have been introduced on the market. A Li-ion battery in an EV can weigh up 450 kg (Tesla roadster), which is a considerable portion of the weight of the whole vehicle (1230 kg) [2]. If the CFRP could be made multifunctional, so as to give structural integrity and energy storing capability, large weight saving could be realized.

This concept of multifunctionality, merging structural composites and batteries, is called structural batteries [3,4,5,6]. A conventional battery consists of two electrodes, with a separating electrolyte in between. In a Li-ion battery, which is the most used battery for EVs today, the positive and negative electrodes consist of a lithium metal oxide and graphite, respectively. Several types of electrolytes exist, including liquids, gels and solid polymers. All of them do, however, contain a lithium salt which is transported between the electrodes during charge and discharge [7].

In earlier studies it has been shown that carbon fibres can perform on par with, or in some respects better than, graphite as negative electrode in Li-ion batteries [8, 9] without much effect on the mechanical properties [10]. This knowledge paves the way to use the carbon fibres both as reinforcement material and as negative electrode. However, to yield a load bearing material, the electrolyte/matrix must consist of a solid polymer of at least moderate stiffness. Since the conductivity of a solid polymer electrolyte (SPE) generally is in inverse relation to the stiffness [11], the design of the battery is crucial. One solution to the poor conductivity of an SPE is to make the electrolyte thinner. An earlier studied approach to prepare a thin electrode (470 nm), utilized electropolymerization to coat CFs individually [12]. However, the polymers used as coating material had a stiffness below 1 MPa, which is unsuitable for a structural composite. Furthermore, more information of the coating surface morphology is needed, especially concerning the existence of pin-holes through the coating.

This study aims to investigate CF coatings utilizing a stiff polymer, with Young's modulus at 320 MPa, to reach closer to a structural battery. Atomic force microscopy (AFM) is used to study the morphology of the coatings in an attempt to find any pin-holes, since a pin-hole would lead to short-circuits in the battery. Additionally, the effect of temperature during coating formation, through electropolymerization, is studied.

2. Materials and methods

2.1 Carbon fibre coating

Carbon fibres were fixed to a frame of 1 mm thick PTFE with a size of 9*2 cm². For the later described AFM experiments, 5-10 fibres were fixed to the frame, while the samples for the rest of the experiments contained 100-300 fibres. The fibres were electrically contacted with copper foil, and were introduced into a glove box with Argon atmosphere (<1 ppm H₂O and O₂). The electropolymerization was performed in a three-electrode electrochemical cell, with the CFs as working electrode, an Aluminium foil as counter electrode and a piece of lithium as reference electrode. The electrodes were submerged in a monomer solution. The monomer solution consisted of either only the monofunctional (mono) methoxy polyethylene glycol (350) monomethacrylate (SR550), monomer or a 60:40 ratio by weight between SR550 and the difunctional (di) tetraethylene glycol dimethacrylate (SR209), kindly supplied by Sartomer Europe. Dimethylformamide (DMF), HPLC grade provided by Fisher Scientific, was used as solvent in a 1:1 weight ratio to the monomers in some monomer solutions. 1 M Li-triflate, purchased from Sigma-Aldrich, was added in all solutions. The CF samples were polarized at 0.2 V vs. the reference electrode (REF) for 300 s according to the procedure in an earlier study [12]. The electrochemical coating was performed using a Solatron SI 1287 potentiostat controlled digitally by Corrware 3.2. After the polarization, the samples were removed from the monomer solution and washed in toluene and dried in room temperature overnight.

2.2 Coating characterization

A number of experimental techniques were used to study the CF polymer coating. Scanning electron microscopy (SEM) was performed at Hitachi S-4800 field emission SEM, to study both surface morphology and CF cross-section. Fourier-transform infrared spectroscopy (FT-IR) was performed using a Perker-Elmer Spectrum 2000 equipped with a heat controlled single reflection “golden gate” unit from Graseby Specac Ltd. The FT-IR was utilized to estimate the curing degree by analysis of the vinyl stretching peak at 1637 cm^{-1} . Thermogravimetric analysis (TGA) The TGA measurements were performed using a Mettler Toledo TGA/DSC 1 STARE System, in which the temperature was increased from $40\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The carbon fibre samples were cut into centimeter-sized pieces and placed in a $70\text{ }\mu\text{l}$ aluminium oxide sample holder. The coating thickness was calculated from the polymer mass determined from the measured weight loss and the known density of the polymer assuming a cylindrical carbon fibre uniformly coated with polymer. An atomic force microscope Nanoscope V, Veeco Instruments (Santa Barbara, CA, USA) was used to examine the surface coating on carbon fibers. One coated fiber was mounted onto freshly cleaved mica and carefully glued in place. The fibers samples were imaged in tapping mode. The instrument was operated at a resonance frequency of 350 kHz and a spring constant of $10\text{-}200\text{ nm}^{-1}$. Height, amplitude and phase images were recorded.

3. Results and discussion

From the FT-IR data (fig. 1) it can be seen that the temperature of the monomer solution during the polymerization process is of importance. The indicated wave number, 1637 cm^{-1} , correlates with the double bond of the methacrylic monomers. That is, a larger peak in this region corresponds to a higher degree of unreacted methacrylic groups [11]. A trend between temperature and the peak at 1637 cm^{-1} can be observed – a lower temperature yields a polymer with higher degree of curing. A possible explanation for this phenomenon is the concept of ceiling temperature. Although the propagation rate of a polymerization reaction increases with temperature, the depropagation rate increases to a higher degree. That is, with an increasing temperature, the depropagation rate will eventually overtake the propagation rate, quenching the polymerization [13]. A lower temperature, will allow the growing polymer chains to propagate further, therefore lowering the unsaturations in the polymer structure.

The impact of the unsaturation in the resulting polymer coating is illustrated by SEM images (fig. 2a-d). A higher temperature, $20\text{-}25\text{ }^{\circ}\text{C}$ (fig. 2a-b) leads to a soft and almost liquid-like substance, most likely partly unreacted monomer, appearing at the cross-section of the coated CFs in the vacuum of the SEM chamber. The samples prepared at a lower temperature, $10\text{-}15\text{ }^{\circ}\text{C}$ (fig. 2c-d), do not present the same amount of softer material at the CF intersection. Instead, a more pristine CF structure can be seen at the CF intersections. This illustrates that a low temperature is essential for the electropolymerization for this given system. The electropolymerization performed at $10\text{ }^{\circ}\text{C}$ yield a polymer coating with low amount of unsaturation, as seen in the IR result, and a solid polymer around each CF. The resulting polymers are believed to reach similar mechanical properties as UV-cured bulk samples prepared from the same monomer system, as shown in an earlier study [11]. Given that, a polymer based only on the monofunctional monomer has a Young's modulus of $<1\text{MPa}$, while a $60:40$ mono:di monomer mixture has 320 MPa , a certain amount of cross-linking difunctional monomer is beneficial for a structural battery application. As a continuation of our earlier study on the system [12], a purely monofunctional solution was tested, albeit

without the solvent DMF. Furthermore a polymerization was performed from a 60:40 mono:di monomer solution, both with and without solvent.

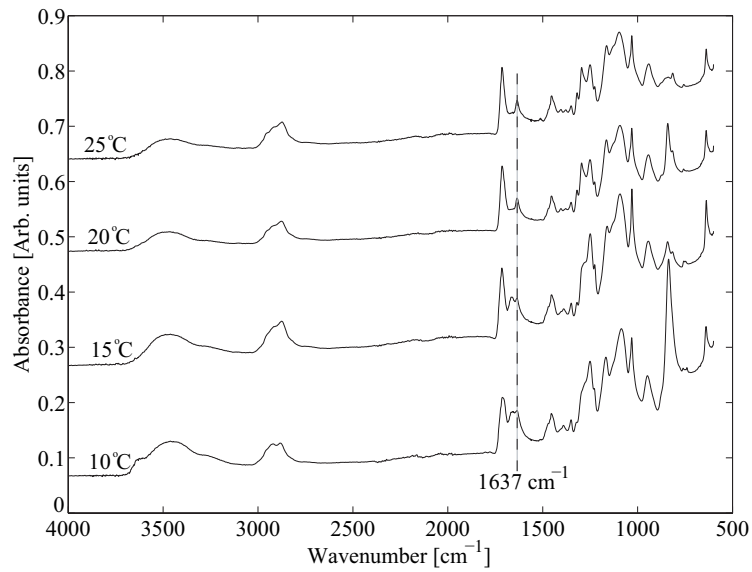


Figure 1. FT-IR spectra for the monomer solution 60:40 mono:di w/o DMF using temperatures of 10-25 °C during electropolymerization. The wavenumber 1637 cm⁻¹ of vinyl stretching is indicated in the figure.

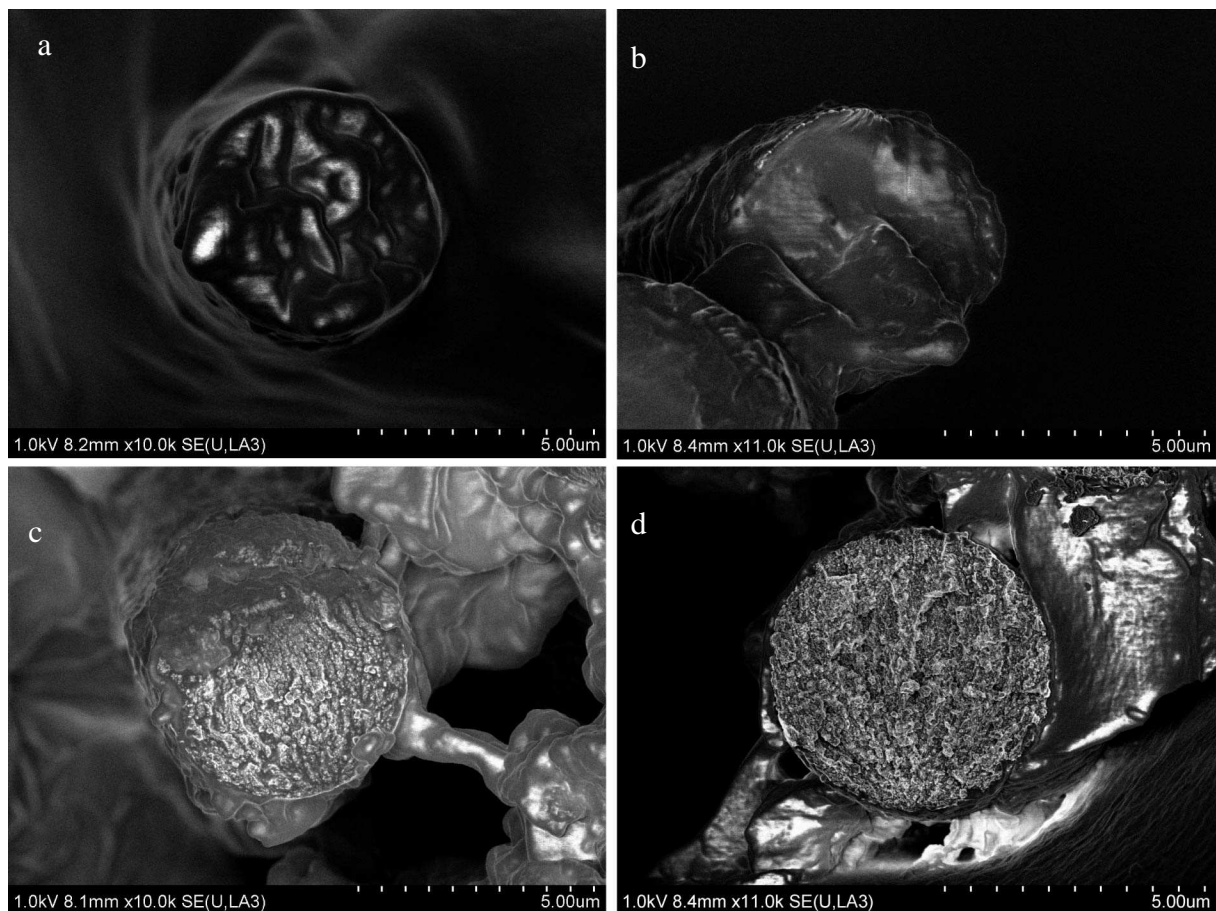


Figure 2. SEM images of the cross-section of CF coated from the monomer solution 60:40 mono:di w/o DMF using temperatures of a) 25 °C, b) 20 °C, c) 15 °C and d) 10 °C during electropolymerization.

It can be seen from the SEM images (fig. 3a-d) that fully covering coatings are produced regardless of monomer solution content. However, only the samples prepared without solvent in the monomer solution (fig. 3a,c,d) can be considered uniform. These three samples do not differ in any distinct manner, as observed in SEM. The coating prepared from 60:40 mono:di and 1:1 monomer:DMF (fig. 3c), on the other hand, show a very rough, almost buckled, surface. This is not optimal for use in a battery, as the distribution in thickness will create an uneven current distribution, possibly reducing the lifetime of the battery. A possible explanation to this uneven surface is that the polymeric coating is created in swollen condition. That is, as the polymer chains grow, DMF is absorbed in the coating structure. When the solvent later evaporates, the structure collapses. This is, however, in contrast with the findings in our earlier study [12] where uniform coatings were prepared from solutions of 100:0 mono:di and a range of monomer:DMF ratios. To explain these differing results, the modulus of the materials becomes important. The very soft (100:0 mono:di) polymer is believed to rearrange its structure during drying of DMF, so as to maintain the smooth surface, while the stiffer (60:40 mono:di) coating is interlocked by the cross-linking. During drying, the material cannot rearrange and thus crumbles and twist producing the uneven surface observed.

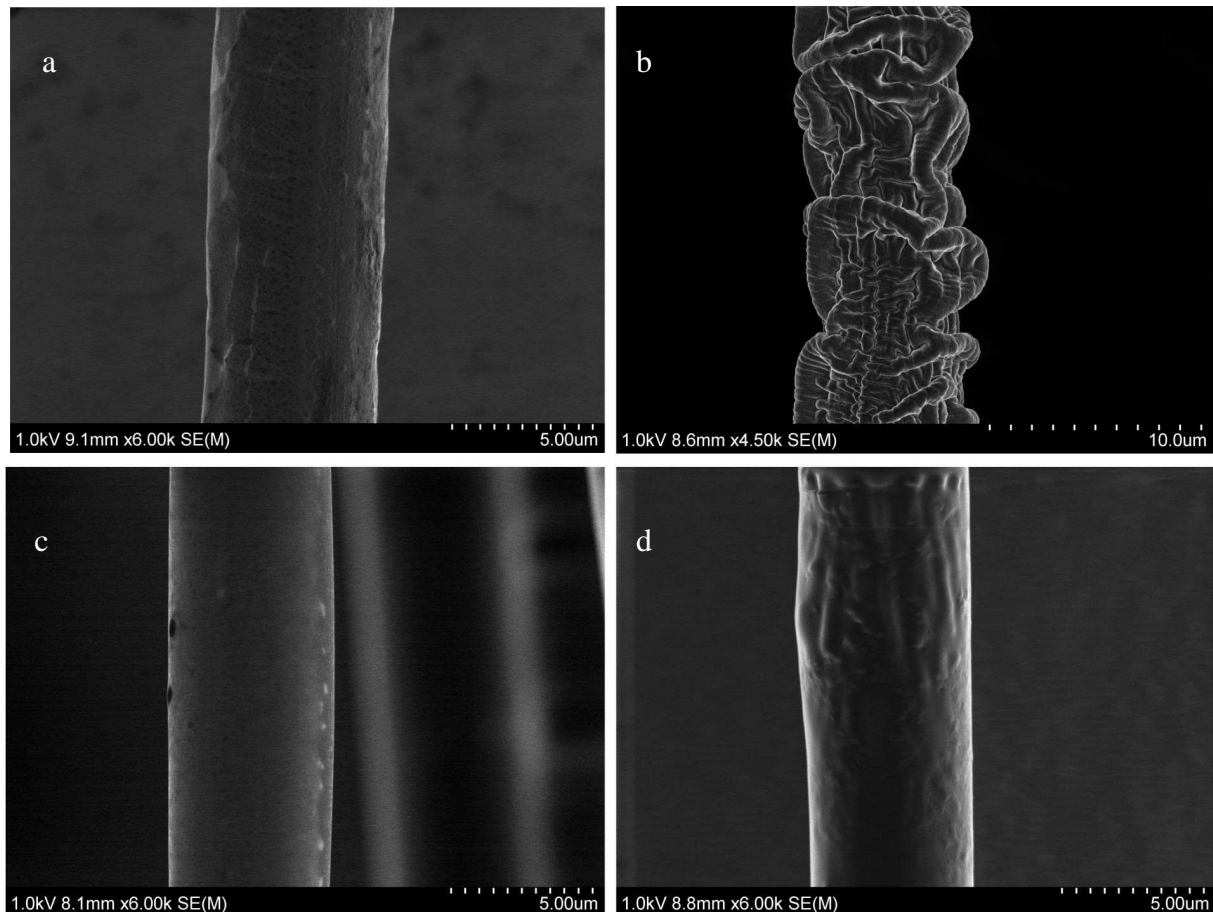


Figure 3. SEM images of the coated surfaces of the CFs using different coating conditions. a) 60:40 mono:di, no DMF, 10 °C, b) 60:40 mono:di, 1-1 monomer-DMF, 10 °C, c) 100:0 mono-di, no DMF, 10 °C, d) 100:0 mono-di, no DMF, 25 °C

To evaluate the polymer thicknesses, TGA was performed on the coated fibres. Assuming a uniform and concentric polymer coating, an estimation of the thickness can be performed. The

resulting estimations (table 1) calculated from the TGA measurements (fig. 4) show a large variation in the thicknesses. The sample prepared with use of solvent (60:40 mono:di 1:1 monomer:DMF) show a thickness (0.5 μm) in line with earlier measurements on monofunctional-based polymers in DMF (470 nm [12]). However, for the samples prepared without solvent, very thick coatings are found. In fact, the values for purely monofunctional-based coatings are in the same order as the diameter of the CFs used (5 μm). From the SEM images of the monofunctionally coated CFs in figure 3a-d where the coatings obviously are not 2-5 μm thick, the assumption that all polymeric material is positioned concentrically around the fibres can be rejected for these reaction conditions.

| | Est. thickness [μm] |
|-------------------------------------|-------------------------------------|
| 100:0 mono:di w/o DMF 25 °C | 5.2 |
| 100:0 mono:di w/o DMF 10 °C | 2.8 |
| 60:40 mono:di w/o DMF 10 °C | 1.9 |
| 60:40 mono:di 1:1 monomer:DMF 10 °C | 0.5 |

Table 1. The estimated thickness, through TGA measurements, for the different reaction conditions

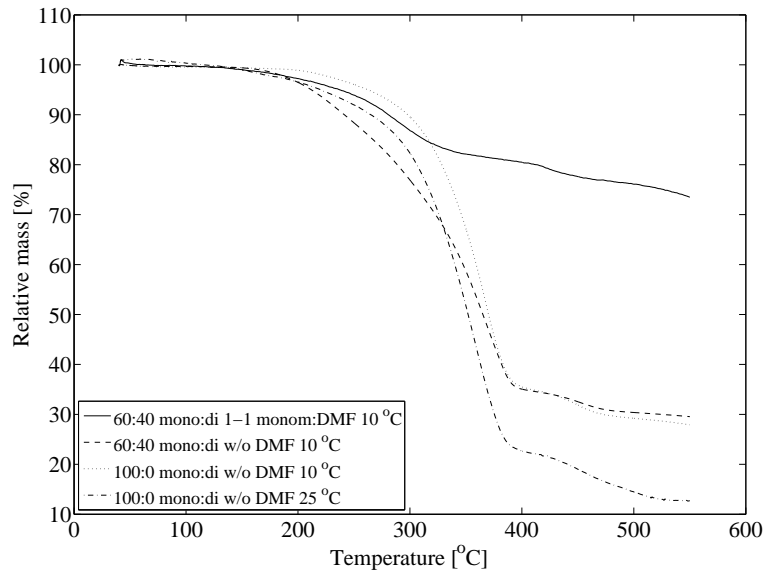


Figure 4. TGA results for the different coating conditions, as indicated in the figure.

The reason for the discrepancy between the TGA and SEM results can be seen in a SEM image of 100:0 mono:di w/o DMF at 25 °C (fig. 5). Although the fibres are coated individually, there is a tendency of the fibres to adhere and almost form a bulk material. The polymer material trapped between the fibres adds to the total mass, making the TGA calculations erroneous. This is believed to be caused by two phenomenon; a thicker coating formed with lower solvent content [12] and a difficulty to rinse excess material after the electropolymerization due to a higher apparent viscosity of the monomer solution.

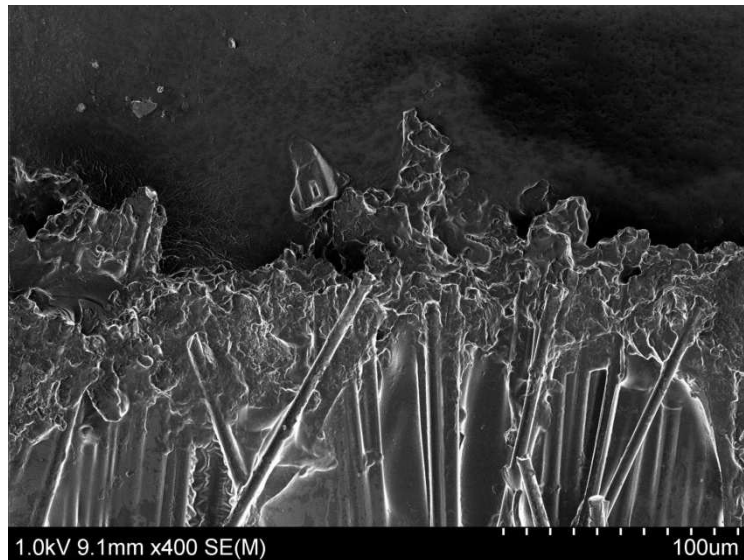


Figure 5. SEM images of the coated surfaces of the CFs from 60:40 mono:di, no DMF, 10 °C. Large amount of fibre-to-fibre adhesion can be seen.

The most important aspect of the CF coating is the separating ability. That is, the carbon fibre (negative electrode) and the electrode particles in the matrix (positive electrode) must be physically separated. If a single pin-hole exists in the coating, the electrodes will touch and a short-circuit will occur, disabling the battery. To investigate this, AFM was used to receive an accurate morphology of the coating surface and to do this in normal atmospheric pressure, avoiding any potential influence of the vacuum used in SEM imaging. A coating prepared in 60:40 mono:di w/o DMF was investigated. The overview of the image was shown in Figure 6 a and b; the detailed view is shown in Figure 6c. The morphology of this coating showed an essentially smooth surface with no pin-holes in the investigated regions. Additional information can be gathered by the phase-part of the data in which brighter areas depict a relatively stiffer material. Even though both SEM and the AFM amplitude results present the coating as smooth and uniform, the phase information show that the material is inhomogeneous on the ~10 nm level (figure 6c). If this behaviour is affecting the function as battery separator is unknown and needs further studies.

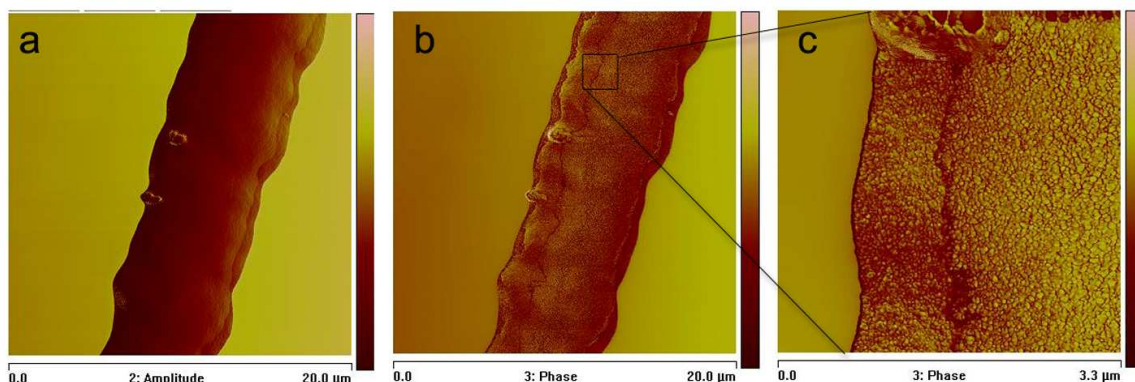


Figure 6. AFM of CFs coated in 60:40 mono:di, w/o DMF, 10 °C, a) Amplitude b) phase image and c) phase image showing the nanostructured coating

4. Conclusions

Within this proceeding it have been shown that it is possible to electrocoat individual CFs with ionically conductive polymers using a mixture of mono- and di-functional monomers. The temperature during the coating process is of great importance, where a lower temperature yielded a more cured coating. The composition of the monomer solution used in the coating process needs consideration so as to achieve sought after result. A uniform coating can be achieved using either a purely mono-functional monomer solution, or a mono-/di-functional mixture using no added solvent, otherwise a very rough polymer surface is formed. However, not using solvent adds the risk of CFs adhering to each other. An AFM study showed a surface without pin-holes, which makes it possible to use the coated CFs as an electrode/electrolyte composite in a structural battery.

5. References

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