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Diamond-like carbon coatings on medically relevant polyurethane tubing with a follow-up aging study

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ABSTRACT

The demands placed on plastics for medical purposes are much higher than for everyday applications. In many cases parent plastic material suits mechanical requirements but exhibits poor surface features, leading to bacterial adhesion and biofilm formation, for instance. This can be avoided by the application of appropriate surface modifications. One frequently used technique is the coating of parent material with functional layers or thin films. The purpose of this study was to demonstrate if medically relevant polyurethane (PU) tubes used for medical products can be coated with a thin diamond like carbon (DLC) film. Samples of raw and sterile material were examined as well as samples which had previously been cleaned with isopropanol. If this alcoholic cleaning does not take place, the resulting carbon coating is unable to adhere to the plastic surface. However, even in the case of clean material the carbon layer starts to deteriorate after five months and has completely broken down within one year, most likely due to internal material stress and/or the appearance of humidity. This implies that the present DLC-coated PU tubes can only be used for a limited length of time. Structural effects and damage appearing close to the surface are shown, using different types of microscopes in a multiscale view as well as follow-up aging studies of the DLC coated tubes.

Keywords: *Diamond-like carbon, polyurethane tubing, surface structure, aging, multiscale microscopy.*

1. INTRODUCTION

Under normal conditions requirements placed on plastics could be varying degrees of flexibility, elasticity, slippage and fracture strength. Plastics used for medical purposes, however, would require long-term stability, durability, chemical resistance and biocompatibility beyond the norm [1]. For example, polyurethane (PU) is commonly used as polymeric material in medical devices due to its exceptional mechanical properties [2]. When, however, PU is used internally, problems such as bacterial adhesion and biofilm formation arise, resulting in infections, even bacterial encrustation [3-5]. There are a number of solutions to overcome these problems. One method of prevention is incorporating active substances into the plastic device [6,7]. Furthermore Wang *et al.* [8] showed that the parent PU-material surface can be covered effectively with bioactive polysaccharide-based multilayers. Either way, the device becomes antibacterial and/or repellent.

Such surface modification can also be achieved on plastic materials by coating them with thin films of diamond-like carbon (DLC) [9-12]. DLC-films are amorphous carbon layers mainly networked of sp^3-hybridized carbon centers but also include contents of sp^2-carbon centers and in some cases fractions of hydrogen atoms. Depending on the deposition method and the resulting composition of carbon centers, DLC shows e.g. varying properties in mechanical hardness [13,14]. Especially higher fractions of hydrogen as well as a lower degree of crosslinking between the carbon species are responsible for a more flexible DLC formation [15]. Recent studies detected the formation of an interlayer between DLC and polyethylene as parent plastic material [10]. Two different types of carbon depositions, one more robust (r-DLC) and one more flexible (f-DLC), were produced in varying thicknesses by plasma enhanced chemical vapor deposition (PECVD), revealing that interlayer formation develops during the first few layers and its dimension depends on the type of DLC [10].

Besides their outstanding mechanical properties, amorphous carbon layers on plastic materials showed excellent biocompatibility and hemocompatibility [3,16-18]. Kleinen *et al.* [4] applied thin layers of amorphous carbon (a-C:H) as well as doped ones to PU ureteral stents, thereby substantially reducing bacterial adhesion, alleviating the problems of crystalline biofilm formation. Moreover several *in vivo* studies revealed a complete absence of encrustations during the indwelling time of the implanted tubes resulting in more comfort for the patients. In *in vitro* experiments Jones *et al.* [3] found that DLC-coated medical polyurethane showed a significant resistance to encrustation and microbial adherence, when carbon layers of lower thicknesses (< 200 nm) are used.

In this study we applied 50 nm of an amorphous, hydrogen containing diamond-like carbon type (a-C:H-type of DLC) [10-12] to PU-tubes, which can be used for artificial nutrition, for instance. The idea is to prevent bacterial growth mechanically on the plastic device by using a specially-treated surface, rendering antibiotics unnecessary. The carbon coating on the tubes was arranged by PECVD. This technique allows the deposition of carbon coatings on materials sensitive to temperature such as soft polymers, because the temperature does not exceed more than 40 °C during the whole deposition process [11]. The surface morphology of the resulting DLC-coatings was analyzed using optical, scanning electron (SEM) and atomic force (AFM) microscopy. Furthermore

the behavior of the DLC-layer relative to the PU surface short-term and long-term was studied.

2. EXPERIMENTAL SECTION

2.1. Material and sample preparation.

The plastic PU-samples studied are of best commercial quality. They are available as sterile polyurethane tubes which are used for medical devices. While some tubes were left untreated and examined as delivered, others were cleaned with isopropanol (IPA) drenched tissues (Kimtech Science, precision wipes No. 7552, Kimberley-Clark®Professional, Kimberley-Clark Europe Ltd., Surrey, UK) and rinsed by running IPA over the tubes to get rid of dust and/or water film. Both uncleaned (= untreated) and cleaned (= treated) tubes were then coated with a 50 nm thin carbon layer (DLC) or left plain as control samples. The differently processed PU-samples are hereinafter referred to as: untreated = sterile raw material; treated = cleaned raw material; uncoated = no DLC layer; coated = with 50 nm DLC layer; the surface morphology of all four possible combinations was studied. After their individual processing the tubes were cut very carefully into pieces of 1 cm length with a scalpel. For better handling the 1 cm samples were cut in half lengthwise and placed outer side facing up on the respective sample holders. The central part of the outer face was analyzed, far enough from the edges so as not to be affected by the cutting. To study effects of aging the prepared samples were stored at room temperature, in ambient air conditions, with no exposure to light and finally analyzed with AFM.

2.2. Coating process.

The tubes were coated with a 50 nm layer of DLC via the method of radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) operating at 13.6 MHz. Weiler *et al.* [19] and Morrison *et al.* [20] give a full description of the applied model COPRA DN 400 (CCR GmbH, Troisdorf, Germany) and an explanation of the basic deposition method can be found in references [4] and [12]. Briefly, in a first process step the untreated and IPA treated tubes are exposed to oxygen plasma for 10 min at about 1 Pa and 200 W of RF irradiation power to remove remaining surface contamination. Afterwards the samples are exposed to acetylene plasma at 0.65 Pa and 107 W. Temperature changes during the deposition process were already determined in an earlier study and never exceeded 40 °C during the entire coating process [11]. During the deposition the PU-tubes hung freely on a rotatable handmade stand, which allows a 360° rotation for each single tube. The stand in turn was mounted on a rotating disk installed at the bottom of the vacuum chamber. The whole set-up is similar to a planetary system and enables an equally thick deposition of carbon layers on the outside of each tube. The thickness of the deposited DLC layer is monitored by 1 cm x 1 cm pieces of silicon wafers, which were partially covered by aluminum foil and additionally mounted near the tubes. The deposition rate for the DLC-layer was determined at 2 nm/min.

2.3. Microscopy techniques for surface characterization.

Optical analysis was conducted using the Keyence Digital VHX 600, under normal conditions as well as using side light illumination to reveal specific characteristics of the polyurethane material and the subsequent carbon coating. Surface morphology of untreated and coated as well as treated and coated samples was analyzed by scanning electron microscopy (Philips XL 30 ESEM, Amsterdam, The Netherlands). The prepared samples were carefully transferred to the sample holders and additionally coated with a few layers of gold (Au) to avoid electron charging effects due to the low conductivity of plastic material. Throughout these experiments the SEM was always operated at an acceleration voltage of 30 kV for the carbon coated samples. Surface studies of treated tubes and of treated and coated ones as well as the aging study of the DLC-layer were done by atomic force microscopy (AFM, Omicron NanoTechnology GmbH, Taunusstein, Germany). These prepared samples were arranged face up onto commercially available AFM sample holders (Omicron NanoTechnology GmbH, Taunusstein, Germany) via an adhesive carbon tape (Plano GmbH, Wetzlar, Germany). Measurements were conducted in contact mode at ambient air conditions with standard silicon nitride PNP-TR cantilevers (NanoAndMore GmbH, Wetzlar, Germany). The recorded normal force signal F_N is shown in every image.

3. RESULTS SECTION

3.1. Before coating.

The optical microscopy examination illustrated in Figure 1 shows the surface topography of untreated PU-tubes (Fig. 1A and Fig. 1C). There are packaging residues (red dotted arrows) as well as remaining dust and mineral particles (black squares and solid white arrows, respectively) clearly visible on the unmodified tube. Furthermore, markings caused by the manufacturing process such as extrusion lines and scratches can be seen. Bumps caused by an uneven melting process, indicated by solid black arrows, shine through from below the surface. After the wiping procedure (= treated) the tube is noticeably cleaner, as shown in Figures 1B and 1D. There are significantly fewer dust particles and no remains of packaging material on the cleaned tube. Compared with the raw material in Figures 1A and 1C even more mechanical damage is detectable in the treated PU-tubing. Scratches are more plentiful in Figure 1B, criss-crossing each other, though shallower, obviously caused by wiping. Bumps (solid black arrows) as well as embedded particles (white circles) are more clearly visible as can be seen in Figure 1D. The cleaning treatment with IPA already shows considerable effects and optical microscopy is sufficient enough to identify macroscopic impurities on the raw sterile tubes very quickly.

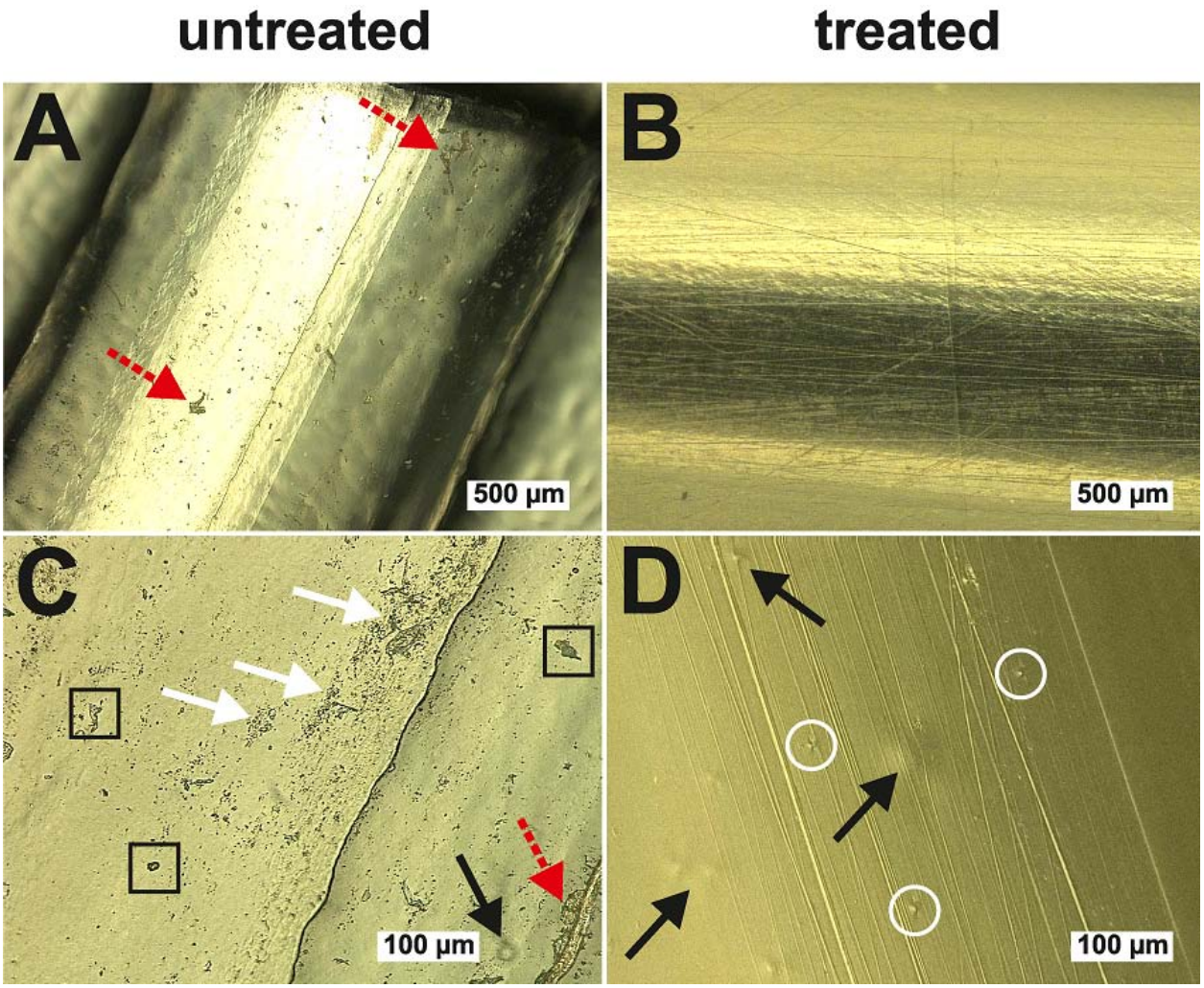

Figure 1. Optical microscopy images of untreated raw PU-tubes (**A** and **C**) and isopropanol treated ones (**B** and **D**) reveal several contaminants (red dotted arrows for packaging material in **A** and **C**, black squares for dust particles and solid white arrows for mineral particles in **C**) and surface characteristics, such as bumps (solid black arrows in **C** and **D**), embedded particles (white circles in **D**) and scratches.

3.2. After coating with DLC.

Both untreated and treated tubes were coated with 50 nm of DLC. Figure 2 shows images of the respective surfaces using optical microscopy, and the images in Figure 3 are of those using SEM. Both microscopy techniques show folding or rolling plates (solid white arrows in Figure 2A/C and Figure 3A), brittleness and broken-off flakes (red dotted arrows in Figure 2A and Figure 3A/C) indicating areas of the carbon layer with no contact to the PU-material. The optical microscopy image in Figure 2A for the untreated and DLC-coated material shows crack lines with spaces in between. The crack lines as well as remaining dust particles are particularly detectable when the method of side light illumination is applied (Figure 2C). Thin crack lines also appear on the treated and DLC-coated material, as illustrated in Figure 2B/D. However, in comparison to Figures 2A/C, they are fewer and farther between, so the number of plates is significantly fewer and the single areas are larger (see Figure 2D). Bumps (white circles in Figure 2B) are still visible, but smoother. The DLC-coating of the cleaned tube in Figure 2B/D appears to cover the main surface features completely.

The SEM images in Figure 3 are consistent with these findings. Those of the untreated coated samples (Figures 3A/C) clearly show irregular cracks in the carbon coating. The DLC layer is breaking off in chunks, displays folded or rolling plates (solid white arrows in Figure 3A) and isolated plates on the surface (red dotted arrows in Figures 3A/C). The material shows a very brittle texture (solid black arrows in Figure 3C) with contaminations of dust particles, which is in line with the findings of the optical microscope (Figures 2A/C). The carbon coating in the SEM-images of the treated tubes (Figures 3B/D) has an overall smooth appearance, still displaying lines and scratches but looking softer due to the coating. Protrusions, possibly dust particles (white circles in Figure 3B/D) seem embedded in the coating. The crack lines are now almost linear, compared to the irregular cracks of the untreated material (Figure 3A/C), and the carbon layer seems to cover them completely undamaged (black dotted arrows, Figure 3D).

The empty spaces of the untreated and coated PU-tubing (Figures 3A/C) indicate brittleness between the carbon layer and the plastic material occurring obviously because of poor adhesion, revealing that no interlayer has formed between these two materials. However, the cleaned tubes show a smooth layer of carbon protecting the parent plastic material fully. This stable covering indicates a strong adhesion to the PU-material with a possible interlayer formation between these two materials.

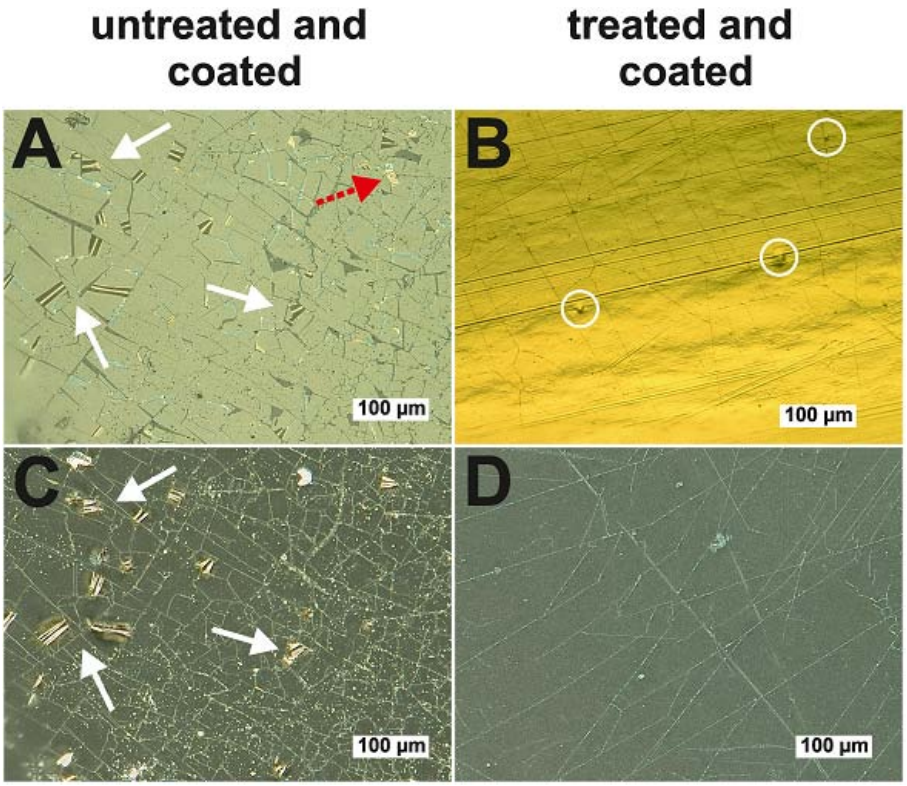

Figure 2. Optical microscopy images of DLC-coated PU-tubes untreated (**A** and **C**) and isopropanol treated (**B** and **D**) display crack lines and surface damage (dotted red arrow for broken-off flakes in **A**, solid white arrows for folding or rolling plates in **A** and **C**) in the DLC-coating. In images **C** and **D** the method of side light illumination is applied for better overview of crack lines and dust particles. The bumps and embedded particles (white circles in **B**) are still detectable although coated with DLC.

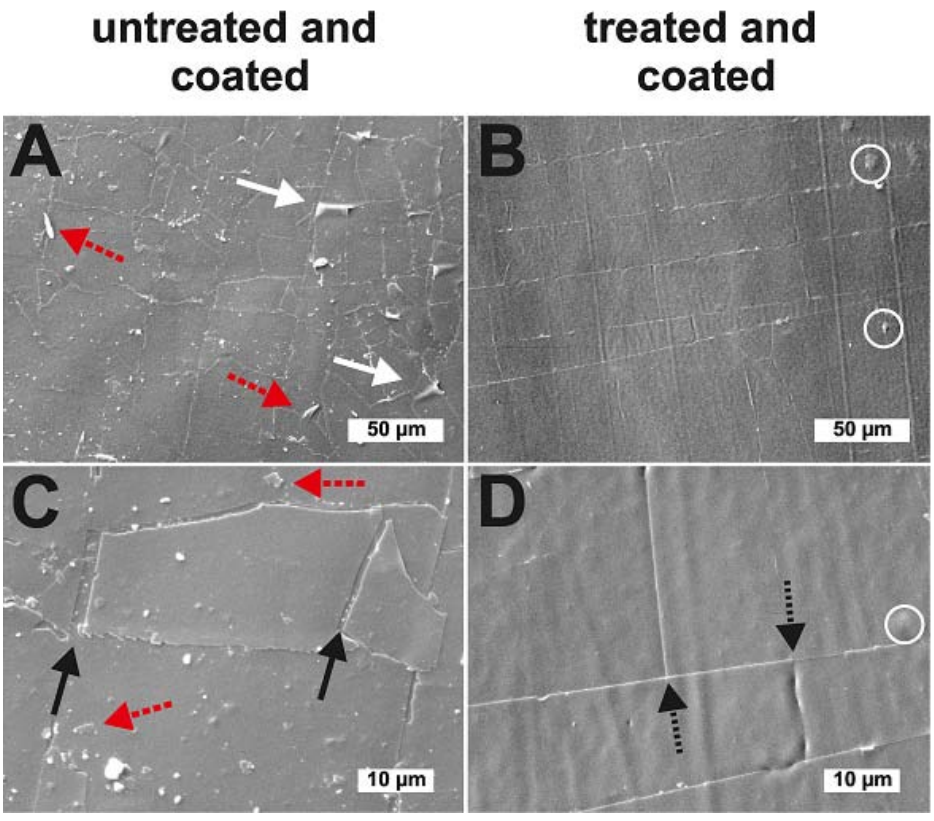

Figure 3. SEM micrographs of DLC-coated PU-tubes untreated (**A** and **C**) and isopropanol treated (**B** and **D**) show crack lines (solid black arrows for cracks with gap in **C**, black dotted arrows for closed crack lines in **D**) and surface damage (red dotted arrow for broken-off flakes in **A** and **C**, solid white arrows for folding or rolling plates in **A**) in the DLC-coating. Bumps of embedded particles (white circles in **B** and **D**) are still detectable in the carbon coating with SEM.

3.3. Aging study.

Atomic force microscopy was chosen for the aging study because SEM-images required a thin conductive layer of gold and it was important to have an uncontaminated surface. Furthermore with this technique it is possible to reveal even smallest changes of the surface morphology in detail due to its small impact and high resolution. Figure 4A displays the topography of a treated PU-tube. The overall contrast in this image is very poor and consistent with the behavior of soft plastic material. There are no significant markings detectable except some presumable bumps or soft irregularities. The diagram on the right shows the profile of the parent PU-tubing with a clean surface (Figure 4A).

The carbon coating on treated material (Figure 4B) shows excellent contrast and reveals significant details after an aging period of up to three months. In the middle of the DLC layer a crack line is visible, possibly due to internal stress or a boundary line between two DLC-plates (Figure 4B). This probably indicates internal material stress or drift especially for the top DLC-layers. Nevertheless, the coating remains entirely on the plastic material because the gap is still filled with carbonaceous material. Adjacent to the plates and on their surface small grain-like spots are visible. The diagram on the right in Figure 4B shows the layered structure of the DLC-coating on the PU-plastic material. Cracks or boundary lines were drawn between the layered structures illustrating the response to internal material stress.

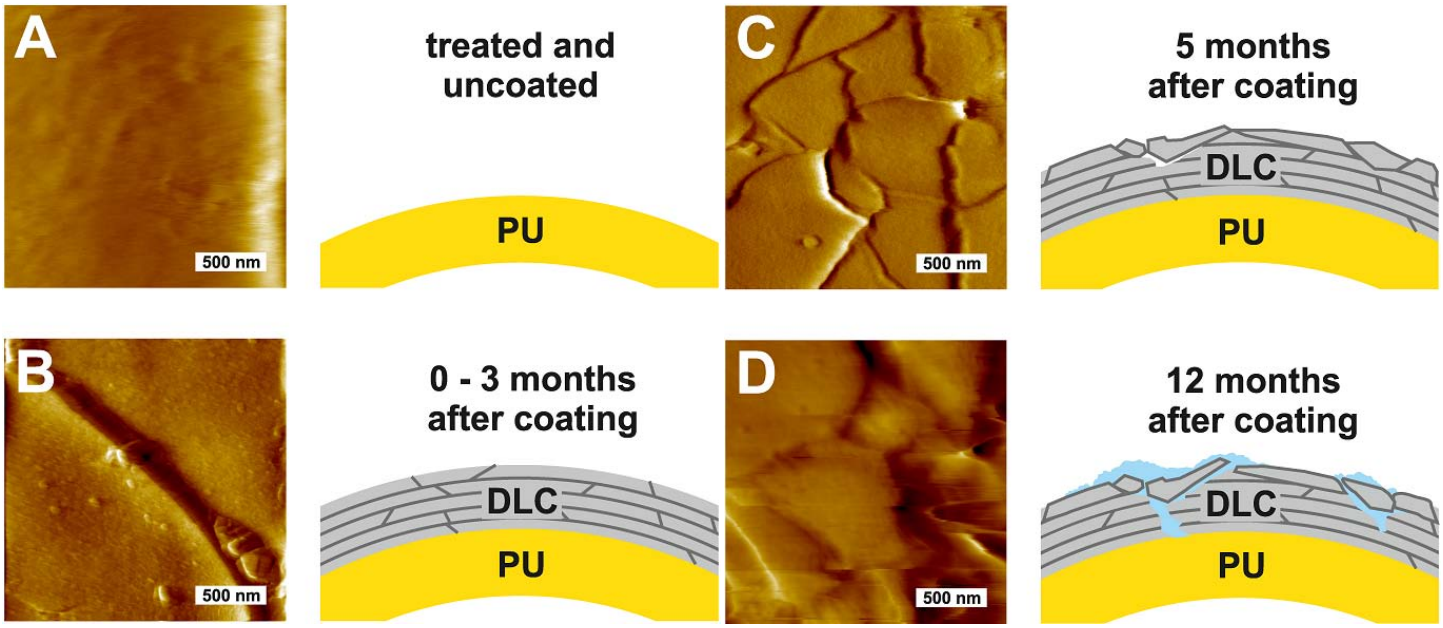

Figure 4. AFM micrographs and diagrams of the PU-DLC material combinations demonstrating the aging process of the DLC-coating on PU-tubes: **A**) treated and uncoated PU-material; **B**) DLC surface up to three months after coating; **C**) DLC five months after coating and **D**) disrupted coating after a period of twelve months.

After an aging period of five months, overlapping flakes become detectable within the same scale of area (Figure 4C). At this stage the DLC-coating has obviously broken down and shows an overall brittle appearance. The cohesion of the carbon layer is lost and the overall surface structure appears like ice floats. The diagram in Figure 4C illustrates the damaged top DLC-layer. The lower carbon layers, however, are most likely still intact and protecting the parent PU-material, because the situation completely changes after a period of 12 months.

In Figure 4D there are still plates recognizable but with 12 months of aging the carbon coating has completely collapsed. Remaining plates are hard to identify and appear like swimming ice floats. The gaps are widely opened and there is no longer contact between the plates. The entire image has poor contrast and shows numerous artefacts. This may arise due to the appearance of humidity either from ambient conditions or from the parent PU-material, which can contain water and/or additives for flexibility [21]. Even if adhesion between the carbonaceous material and the PU-plastic right after the coating was good because the water film had been removed by the oxygen plasma, incorporated substances may migrate to the tubes surface and damage the coating. Water can also be attracted from surrounding air and penetrate the gaps between the plates and the DLC-layer deteriorates (Figure 4D). The carbon layer has completely broken down; there is no longer protection of the plastic material. Water and other contaminants can now penetrate the carbon layer very easily from either direction. The diagram illustrates the broken down carbon layer and the lack of protection of the plastic material.

4. CONCLUSIONS

Images of treated and untreated DLC-coated PU-plastic tubing from two types of microscopes revealed that failing to clean the surfaces before coating renders them unsuitable for use due to lack of adhesion. The sterile raw material must first be

cleaned with isopropanol to remove packaging, dust particles and other impurities before coating with DLC so as not to suppress adhesion and presumably interlayer formation to the parent PU-tubing material. PU-samples which were successfully coated with DLC showed good adhesion of the carbon layer to the parent plastic material. Aging studies of these analyzed by AFM revealed the coherence of the deposited DLC layer to the IPA pretreated plastic material over a period of twelve months. For up to three months the DLC coverage completely protects the parent material although showing effects of internal material stress in the form of fine crack lines, but without gaps. Over time the DLC layer becomes more and more brittle, breaking of in numerous overlapping flakes. After twelve months the carbon coating has completely deteriorated, presumably because of attracting water from surrounding air and/or the migration of plastic ingredients to the materials boundary. No persistent DLC-coating was achieved long-term for the present tubes by applying the current parameters, indicating a weak and thin or even no interlayer formation between these two materials.

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