Preparation techniques of thin cyanoacrylate adhesive films for interface analysis

Philipp Moritz, Friedrich Bürger, Lienhard Wegewitz, and Wolfgang Maus-Friedrichs

Clausthal Center for Material Technology, Clausthal University of Technology, Clausthal-Zellerfeld, Germany

ABSTRACT
For understanding the interactions between adhesives and different surfaces, the in-situ characterization of the interface is essential. Especially for highly reactive cyanoacrylates, better known as super glues, the adhesion mechanism is poorly understood because, among other things, the characterization of the interface is difficult. The aim of this work is to evaluate methods to produce nm-thin, homogeneous films of cyanoacrylate to enable spectroscopic analysis of the interface in the future. Two deposition techniques, thermal evaporation and spin coating, of ethyl-cyanoacrylate, are compared. Thickness and composition of the cured films are investigated by atomic force microscopy, laser scanning microscopy and x-ray photoelectron spectroscopy. Thermal evaporation in ultra-high vacuum leads to cluster-like depositions and is therefore not suitable for interface analysis. Spin coating is strongly dependent on solvent and concentration. While the solvent tetrahydrofuran leads to porous and inhomogeneous films, spin coating with anisole as solvent provides homogeneous films of cyanoacrylate with a thickness of only 4 nm. This allows surface-sensitive analytical methods to access the interface and possible interactions can be characterized in-situ.

1. Introduction
Cyanoacrylates are the main component of fast curing adhesives, commonly known as ‘superglues’. These adhesives have a wide range of commercial applications, e.g. joining hybrid materials in industry,[1,2] exposure of invisible fingerprints in forensic science,[3,4] as a bio-adhesive in the biomedical field,[5,6] but also as a domestic adhesive. The monomer unit of cyanoacrylates is shown in Figure 1.

The rest -R represents methyl, ethyl and longer-chain alkyl groups. These influence the curing time and the physical and mechanical properties of the polymer.[7] The curing mechanism has already been studied in numerous publications and identified as an anionic polymerization. The initiating
Figure 1. Structural formula of a cyanoacrylate monomer.

anion is usually a hydroxide ion that originates from the surrounding humidity or water molecules adsorbed on the surface of the materials to be joined.\cite{8,9}

Although cyanoacrylates already exist on the world market for several decades and the chemistry behind the curing process is already well researched, there are hardly any studies on the exact bonding mechanism between cyanoacrylate and adherent surfaces. This lack of research on the complex topic of adhesion also exists for numerous other adhesive/adherent surface combinations. Classical methods of surface analysis are well suited to investigate, for example, the adhesion between cyanoacrylate and metallic joining partners. For instance, X-ray photoelectron spectroscopy (XPS) can detect chemical bonds and ultraviolet photoelectron spectroscopy (UPS) allows the investigation of adsorbed species and the valence band. However, the information depth of these methods is only a few nanometers. A major challenge in the in-situ investigation of adhesion is therefore the preparation of the specimen in order to make the interface accessible to the characterization techniques.

A common approach in the literature is the evaporation of metals on polymer substrates.\cite{10–13} However, it is questionable to what extent the interaction of a liquid adhesive with the metal is related to the interaction of evaporated metal atoms with the cured adhesive. A technique that better represents reality is the deposition of thin polymer or adhesive films on a metal substrate. Possart and Schlett\cite{14} dissolved already polymerized PMMA in acetone and used a spin coating method to deposit thin PMMA films on aluminum and gold surfaces. The adjustable film thickness from a few nanometers to a few hundred nanometers allowed them to study interfacial interactions with XPS. Possart and Dieckhoff\cite{15} used a very similar procedure to study the adhesion of cyanurate polymers on silicon and aluminum with XPS and UPS. They used a combination of spin coating and molecular beam deposition.

For cyanoacrylates, no comparable interface investigations using XPS or UPS could be found. Kusaka and Suëtaka\cite{16} placed an aluminum oxide substrate over liquid cyanoacrylate monomer and were able to deposit several monolayers by evaporation at room temperature. While they did not specify exact layer thicknesses, they observed band shifts of the carbonyl and ester groups in IR spectra and assume a formation of hydrogen bridge bonding
between cyanoacrylate and aluminum oxide. Based on this work, Reynolds et al.\textsuperscript{[17]} deposited cyanoacrylate films on aluminum oxide and investigated the adhesion by inelastic electron tunnelling (IET). They tested different preparation methods, but could not find a more suitable technique for the IET method than the one already proposed by Kusaka and Suëtaka.\textsuperscript{[16]} Problems included the high reactivity of cyanoacrylate and residues of solvent on the surface.

In order to enable the analysis of the interface between cyanoacrylate and an adherent surface, the two methods of spin coating and thermal evaporation will be investigated in more detail in this work. Thickness and uniformity of the deposited films are examined by atomic force microscopy (AFM) and confocal laser scanning microscopy (CLSM). The chemical composition and binding species of the adhesive films are analyzed by X-ray photoelectron spectroscopy. The aim is to create homogenous cyanoacrylate films from 4 nm to 10 nm thickness, which allows the investigation of differences in adhesion at the interface of cyanoacrylate and adherent surfaces by XPS and other surface-sensitive methods in the future.

\section{Materials and methods}

\subsection{Sample preparation}

For the different deposition techniques in this work, Si (100)-wafers (polished and n-doped, Crystec, Berlin, Germany) with a size of $10 \times 10 \times 0.625$ mm$^3$ were used as substrate. They have a root mean squared roughness of $<1$ nm and are therefore well suited to deposit homogenous adhesive films with a thickness of a few nanometers. The wafers were previously cleaned in isopropanol (Sigma-Aldrich, Taufkirchen, Germany) in an ultrasonic bath for 10 minutes each, shaken out in distilled water and allowed to dry. A commercial instant adhesive (Loctite 401, Henkel, Dusseldorf, Germany) was used for all experiments. According to the manufacturer’s specifications, it contains ethyl-cyanoacrylate as the main component.

In order to determine whether the two deposition techniques affect the chemical composition and binding structure of the cyanoacrylate, reference measurements were first carried out. For this purpose, 500 \mu l of the commercial adhesive was applied directly onto the wafer with a pipette. The thick adhesive film had sufficient time to fully cure and dry before further examination. A total of three samples were prepared in this manner and analysed to provide a reliable reference.

The evaporation experiments were carried out with a thermal evaporator (TCE-BSC, Kentax, Seelze, Germany). The evaporator was operated in vacuum at a pressure below $2 \cdot 10^{-6}$ mbar. It contains a heatable quartz glass crucible that was filled with the commercial cyanoacrylate and was outgassed for 2 hours at 100°C and 5 minutes at 190°C. This step is crucial to remove
water and possible contaminations. Afterwards, the adhesive was heated to temperatures between 195°C and 205°C and evaporated onto the cleaned Si wafer for 5 to 30 minutes. Several evaporation steps with different times and temperatures were carried out consecutively in order to measure a gradual growth of the layer.

The spin coating experiments were performed on a commercial spin coater (WS-650-23B, Laurell Technologies, North Wales, USA). The uncured cyanoacrylate was dissolved in tetrahydrofuran (THF, ≥99.9%, Sigma-Aldrich, Taufkirchen, Germany) or anisole (≥99.7%, Sigma-Aldrich, Taufkirchen, Germany) in different concentrations, respectively. 40 µl of the adhesive solution were dropped onto a resting wafer and immediately rotated at different speeds for 60 s. Acceleration to the final speed took place within 1 s. Table 1 shows the tested combinations of solvent, concentration and rotation speed.

### 2.2. Characterization methods

After deposition, some selected samples were analyzed using X-Ray Photoelectron Spectroscopy. All XPS measurements were performed in an ultra-high vacuum chamber (UHV) with a base pressure below $3 \cdot 10^{-10}$ mbar. The exact setup of the UHV system used was described previously.\cite{18,19} The transfer between thermal deposition and the investigation by XPS took place without interruption of the UHV conditions. A commercial X-ray source (RS40B1, Prevac, Rogów, Poland) was used to generate non-monochromatic AlKα X-rays (1486.6 eV) that hit the surface at an angle of 80° to the sample normal. The emitted photoelectrons were recorded by a hemispheric analyzer (EA10/100, Leybold, Cologne, Germany) at 10° to the sample normal. Survey spectra were measured with a pass energy of 80 eV and for detail peaks at least 10 spectra each was recorded at a pass energy of 40 eV and arithmetically averaged. The quantitative and qualitative analysis of the XPS spectra was performed with the software CasaXPS. It allows a precise fit of the peaks with the Levenberg-Marquardt algorithm, assuming a Tougaard background correction. The XPS spectra are displayed as a function of binding energy with respect to the Fermi level. Due to the poor electrical conductivity of the

| Sample | Solvent | Concentration of cyanoacrylate in wt.-% | Rotation speed in rpm |
|--------|---------|----------------------------------------|-----------------------|
| 1      | THF     | 0.2                                    | 5000                  |
| 2      | THF     | 0.5                                    | 5000                  |
| 3      | THF     | 2.0                                    | 5000                  |
| 4      | THF     | 5.0                                    | 5000                  |
| 5      | Anisole | 1.0                                    | 5000                  |
| 6      | Anisole | 2.0                                    | 5000                  |
| 7      | Anisole | 10.0                                   | 3000                  |
adhesive, a charge correction was applied and the C-C binding was referenced to 285.0 eV in all spectra.

The topography and thickness of the thin adhesive film were examined with an Atomic Force Microscope (Dimension 3100, Veeco Instruments, Santa Barbara, USA). It was operated under atmosphere in tapping mode with aluminum-coated silicon cantilevers (NSC15/Al BS, Micromasch, Wetzlar, Germany). They have a spring constant of about 40 N/m and a resonance frequency in the range of 325 kHz. Each image consists of 512 lines and was recorded at a line-scan frequency of 0.5 Hz. In order to analyze the film thickness, a steel syringe needle was used to insert a scratch into the coating and then the depth of the scratch was measured. By scratching a pure Si wafer, it was ensured that only the adhesive is removed during this process and the wafer is not damaged. The depiction and possible tilt corrections of the images were performed with the SPIP 6.1.1 software (Image Metrology).

The thickness and topography of the reference film were examined with a Confocal Laser Scanning Microscope (VK-X200K, Keyence, Neu-Isernbürg, Germany). It works with laser light of the wavelength 408 nm at a power of 0.95 mW and enables images with a high depth of focus. The manufacturer specifies a reproducibility of ±12 nm for a height measurement on a 2 μm high step. The analysis of the images was performed with the Keyence Analysis Software (Version 3.2.0.0).

3. Results and discussion

3.1. Application by dripping

When applied by dripping on, the cyanoacrylate wets the Si wafer evenly and forms a macroscopically homogeneous film. The introduction of the scratch into the cured polyethyl-cyanoacrylate (PECA) film produces numerous splinters, which indicates a brittleness of the coating. Figure 2 shows a CLSM image of the sharp edge between intact adhesive film and Si wafer. Several profile measurements of the fracture give an average film thickness of (3.71 ± 0.37) μm, which is significantly higher than the information depth of XPS. The mean square roughness of the cyanoacrylate film, measured with AFM on three 20 × 20 μm² areas, is (0.45 ± 0.02) nm.

All XPS measurements of an intact film show the signals of carbon (68.2 ± 1.0 at.-%), oxygen (28.5 ± 0.9 at.-%) and nitrogen (3.3 ± 0.2 at.-%), which are distinctive of the adhesive. As was to be expected with the high film thickness, the underlying Si substrate cannot be detected. The measured stoichiometry does not match the theoretical values for PECA (66.7 at.-% carbon, 22.2 at.-% oxygen and 11.1 at.-% nitrogen), which may be due to the presence of unknown additives in the commercial adhesive or atmospheric contamination on the sample surface.
The XPS detail spectra of the C1s, O1s and N1s peak are shown in Figure 3. As can be seen from the structural formula of the ethyl-cyanoacrylate monomer unit in Figure 4, the adhesive contains characteristic functional groups and chemical bonds that allow the detail peaks to be deconvoluted. Due to the lack of literature on XPS of cyanoacrylates, measurements of chemically similar substances like poly-methylmethacrylate (PMMA), poly-ethylmethacrylate (PEMA) and poly-acrylonitrile (PAN) were used for evaluation.\[14,20,21]\n
The C1s detail spectrum (Figure 3, left) can be fitted very well with five different carbon species: (1) aliphatic C-C/C-H at 285.0 eV, (2) aliphatic C-C with an energy shift at 285.7 eV due to the influence of the adjacent oxygen and nitrogen, (3) C-O at 286.8 eV, (4) C≡N at 286.7 eV and (5) O=C-O at 288.9 eV. Considering the monomer unit in Figure 4, these carbon species should theoretically have a ratio of 2:1:1:1:1. However, as the
deconvolution in Figure 3 shows, the measured ratios do not fully coincide. As already stated in the discussion of stoichiometry, this is probably due to additives or contamination on the surface. The oxygen (i, ii) and nitrogen (a) containing species can also be found in the corresponding O1s and N1s detail spectrum in Figure 3. The PECA thus shows distinctive peaks in the XPS measurements, which is used as a reference for the quality of the deposited films after thermal evaporation and spin coating. One of the samples was exposed to X-rays for 150 min and no significant changes in detail peaks were observed. Damage to the chemical bonds of the polymer by X-rays during the measurement can therefore be excluded.

### 3.2. Thermal evaporation

Preliminary to the actual evaporation experiment, the Si wafer was cleaned and heated in the UHV to remove possible contamination. The success of the cleaning procedure is proven by the stoichiometry of the surface shown in

![Figure 4. Monomer unit of PECA.](image.png)

#### Table 2. Stoichiometry of the surface after each evaporation step determined by XPS.

| Evaporation step | Carbon in at.-% | Nitrogen in at.-% | Oxygen in at.-% | Silicon in at.-% |
|------------------|-----------------|------------------|----------------|-----------------|
| Cleaned wafer    | 1.9             | -                | 39.5           | 58.6            |
| + 195°C, 5 min   | 13.0            | 0.7              | 35.8           | 50.5            |
| + 195°C, 10 min  | 24.5            | 1.2              | 33.7           | 40.9            |
| + 200°C, 10 min  | 37.4            | 2.9              | 31.2           | 28.5            |
| + 200°C, 15 min  | 45.9            | 3.0              | 30.3           | 20.8            |
| + 205°C, 10 min  | 51.6            | 2.5              | 29.0           | 16.9            |
| + 200°C, 30 min  | 57.1            | 3.4              | 28.1           | 11.4            |
Table 2. Besides the signals of oxygen and silicon, only very small traces of carbon can be found. The detail spectra of the Si 2p peak in Figure 5 (left) show a splitting into two species at 99.8 eV and 103.6 eV, which can be assigned to the oxidation states of metallic silicon (0) and silicon dioxide (4+), respectively. \[22\] This means that the Si wafer is initially covered by an oxide layer of a few nanometers onto which the adhesive is thermally evaporated. Table 2 also shows the stoichiometry of the sample surface after each of the evaporation steps that were performed in consecutive order. While the silicon signal decreases with evaporation time, the carbon and nitrogen signals characteristic of cyanoacrylate increase almost continuously. In the case of oxygen, the proportions of silicon oxide and adhesive overlap.

In order to verify whether the deposition is cyanoacrylate, detailed measurements were performed. The C1s detail peak (Figure 5, right) forms a characteristic structure with increasing evaporation time. The peaks can be deconvoluted with the same species as the reference film in Figure 3. However, the ratio of intensities between the species differs significantly from the reference sample. Especially the small proportion of the O-C=O group at 288.9 eV is evident. The elevated temperatures around 200°C and the long evaporation time of 80 min could have damaged the chemical bonds and thus changed the polymer structure. However, it is also noticeable that despite longer evaporation times and temperatures, less and less adhesive is deposited, i.e. the deposition rate is decreasing.

An ex-situ observation of the surface using AFM indicates that no uniform and homogeneous cyanoacrylate film was deposited on the wafer. Figure 6(a) shows a 5 x 5 µm² section of the surface, a corresponding 3D view (b) and a line profile measurement (c). Elongated, oval structures with a length of 1 µm to 3 µm and a width of 0.5 µm to 1 µm are visible on the entire surface. The height varies from about 100 nm to 250 nm. Between these structures, the smooth Si wafer surface is nevertheless clearly visible. For comparison, Figure
Figure 6. (a) 5 × 5 µm² AFM image of the Si wafer surface after an evaporation time of 80 min; (b) 3D representation of the image in (a); (c) corresponding height profile to the line in (a).

7(a) shows the surface of a second sample with cyanoacrylate evaporated for a shorter time of 18 min. Here, very similar structures appear, but they are less dense and narrower. The line profile measurement in Figure 7(c) shows lower heights of 40 nm to 110 nm. The 3D representation in Figure 7(b) indicates that a large area of the Si wafer is still uncovered.

These observations are supported by the XPS measurements. At the beginning of the evaporation process, many of these polymeric structures are formed. However, with longer evaporation times, these structures do not grow together to form a homogeneous film, but instead grow upwards. Only very long evaporation times would probably cause the structures to touch each other and a closed film may be formed. The Si wafer therefore remains measurable with XPS even after longer evaporation times.

Reynolds et al. [17] reported on ‘polymer mounds’ during their evaporation experiments of ethyl-cyanoacrylates under a normal atmosphere. They explained this growth pattern with traces of moisture in the atmosphere and on the substrate, which served as a nucleus for the formation and further polymerization of the adhesive. They solved the problem with an SO₂- or N₂-containing atmosphere, which led to more homogeneous films.
However, the situation here is different, since the experiments were carried out in UHV at a pressure of $10^{-7}$ mbar and the wafer surface and crucible were previously heated and cleaned. Furthermore, the cyanoacrylate is probably already completely cured before it is evaporated. Another explanation could be the wetting behavior of the hot polymerized adhesive on the oxidized wafer surface. Additional experiments on other surfaces, e.g. purely metallic surfaces, would have to be carried out to determine the influence of the interfacial tension.

### 3.3. Spin coating

The topography of the spin coating films with THF as a solvent was investigated by AFM. Figure 8 shows $20 \times 20 \, \mu m^2$ images of four different concentrations of cyanoacrylate, each displaying the transition area between intact coating and uncoated Si wafer. However, none of the investigated concentrations lead to a homogeneous adhesive film. Especially at lower concentrations of 0.2 wt.-% and 0.5 wt.-% cluster-like structures become visible, between which the smooth wafer can be clearly recognized. With increasing
concentrations of cyanoacrylate, the clusters become denser and form a closed film, but the granular and inhomogeneous structure remains. The height of the structures at the low concentration of 0.2 wt.-% to 2.0 wt.-% does not change significantly and is 30 nm to 40 nm. Only the solution with 5.0 wt.-% ECA leads to an increased layer thickness of 60 nm to 70 nm. Thus, none of the THF solutions produces a sufficiently thin and homogeneous film that allows XPS measurements of the interface.

Reasons for the observed structures could be a premature polymerization of the adhesive in the solvent. The THF as a cyclic ether does not act as the initiator of the reaction. Experiments with a second batch of THF led to the same results, so moisture in the solvent can presumably be excluded. Vorotilov et al.[23] investigated the influence of temperature on the topography and thickness of spin coated films. They found that a high evaporation rate of the solvent leads to porous and increasingly thicker films. It could be that the THF evaporates too quickly in the spin coating process due to the high vapor pressure. As a result, the cyanoacrylate cannot form a homogeneous film, but cures in a porous and inhomogeneous structure.

The spin coating films with anisole as solvent were also examined by AFM. Again, the $20 \times 20 \mu m^2$ images in Figure 9 show the transition area between coated and uncoated wafer for different concentrations and rotation speeds. Compared to THF, the closed films are much more homogeneous and smooth. Moreover, with decreasing concentration, they do not become porous, but instead, the film thickness decreases evenly.

Figure 10 shows the XPS survey spectra of the spin coating films with (a) 10 wt.-% at 3000 rpm and (b) 2 wt.-% and 5000 rpm. The determined layer thicknesses of (a) 20.0 nm and (b) 4.3 nm are above and below the XPS information depth of about 10 nm, respectively. This is also reflected in the element signals found. The thick film shows signals of carbon (66.1 at.-%), oxygen (30.4 at.-%) and nitrogen (3.5 at.-%) and thus has approximately the same stoichiometry as the reference sample of the dripped film. The thin film, on the other hand, shows not only the signals of carbon (39.9 at.-%), oxygen (32.6 at.-%) and nitrogen (3.9 at.-%), but

Figure 8. $20 \times 20 \mu m^2$ AFM images of spin coating films with THF as a solvent. Top: Different concentrations of ethyl-cyanoacrylate.
also a significant amount of silicon (23.7 at.-%) originating from the substrate. The signals from the cyanoacrylate film and oxidized wafer overlap and allow XPS to detect the interface and possible chemical bonds.

In order to verify that the films are indeed polyethyl-cyanoacrylate, detailed spectra were recorded. Figure 11 shows the C1s detail spectrum of the thick film.
with 10 wt.-% at 3000 rpm. The peak has the same structure as the reference measurement in Figure 3 and can be deconvoluted with the same carbon species (1) to (5). Table 3 shows the relative amount of each carbon species in comparison to the reference measurement. The differences in the proportions are small and there are no additional species such as aromatic carbon bonds that would indicate the presence of anisole in the film. It can therefore be assumed that the thin homogeneous film is the commercial polyethyl-cyanoacrylate.

**Figure 11.** XPS detail spectrum of the C1s region of the spin coating film with 10 wt.-% PECA in anisole at 3000 rpm.

**Table 3.** Relative amounts of carbon species in C1s detail peak of the reference sample and the spin coating film (10 wt.-% ECA in anisole at 3000 rpm).

| Carbon species | Reference sample | Spin coating film |
|----------------|------------------|-------------------|
| (1) C-C/C-H    | 41.0%            | 43.7%             |
| (2) C=C/C-H, shifted | 19.2%            | 18.2%             |
| (3) C-O        | 10.3%            | 10.0%             |
| (4) C≡N        | 10.2%            | 9.9%              |
| (5) O=C-O      | 19.3%            | 18.2%             |
4. Conclusion

The two deposition techniques of thermal evaporation and spin coating were investigated to enable surface analytical methods to access the interface between a closed cyanoacrylate adhesive film and adherent surfaces in the future.

During thermal evaporation, the polyethyl-cyanoacrylate did not form a homogeneous film on the wafer, but granular structures reaching heights of several hundred nanometers. XPS measurements also showed changes in the binding structure in the polymer. Thus, the thermal evaporation method is not suitable to produce cyanoacrylate films that would allow the investigation of the interface. However, it cannot be excluded that the deposition on surfaces other than the oxidized wafer is different. Experiments are therefore planned to investigate deposition in ultra-high vacuum on pure metals.

The results of the spin coating depend strongly on the selected solvent and the concentrations of the cyanoacrylate. The solvent anisole has a suitable vapor pressure and does not remain in the produced film. Thus, films could be produced which will allow the analysis of the adhesion with surface analytical methods such as XPS and UPS in the future. Within the research project, the adhesion of cyanoacrylates on different metals and the corresponding metal oxides will be investigated in the future by means of an atmosphere free of oxygen and water vapor (partial pressure of oxygen $<10^{-23}$ bar).

Acknowledgements

The authors thankfully acknowledge the provision of the AFM by Prof. W. Daum and CLSM by Prof. F. Endres.

Funding

This research has been funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 394563137 – SFB 1368.

ORCID

Philipp Moritz http://orcid.org/0000-0002-7582-101X

Declaration of interest

The authors declare no conflict of interest.
References

[1] Mazur, P.; Evaluation of the Quality of Cyanoacrylate Adhesive Joints Using the Example of Poly(methyl Methacrylate) and Polycarbonate. PEA. 2017, 14, 7–10. DOI: 10.30657/pea.2017.14.02.

[2] Shantha, K. L.; Thennarasu, S.; Krishnamurti, N. Developments and Applications of Cyanoacrylate Adhesives. J. Adhes. Sci. Technol. 1989, 3, 237–260. DOI: 10.1163/156856189X00191.

[3] Czekanski, P.; Fasola, M.; Allison, J. A Mechanistic Model for the Superglue Fuming of Latent Fingerprints. J. Forensic Sci. 2006, 51, 1323–1328. DOI: 10.1111/j.1556-4029.2006.00258.x.

[4] Wargacki, S. P.; Lewis, L. A.; Dadmun, M. D. Understanding the Chemistry of the Development of Latent Fingerprints by Superglue Fuming. J. Forensic Sci. 2007, 52, 1057–1062. DOI: 10.1111/j.1556-4029.2007.00527.x.

[5] Korde, J. M.; Kandasubramanian, B. Biocompatible Alkyl Cyanoacrylates and Their Derivatives as Bio-adhesives. Biomater. Sci. 2018, 6, 1691–1711. DOI: 10.1039/c8bm00312b.

[6] Masood, M. T.; Zahid, M.; Goldoni, L.; Ceseracciu, L.; Athanassiou, A.; Bayer, I. S. Highly Transparent Polymethylcyanoacrylates from Approved Eco-Friendly Fragrance Materials Demonstrating Excellent Fog-Harvesting and Anti-Wear Properties. ACS Appl. Mater. Interfaces. 2018, 10, 34573–34584. DOI: 10.1021/acsami.8b10717.

[7] Lees, W. A.; The Science of Acrylic Adhesives. Br. Polym. J. 1979, 11, 64–71. DOI: 10.1002/pi.4980110206.

[8] Pepper, D. C.; Zwitterion Chain Polymerizations of Cyanoacrylates. Makromolekulare Chemie. Makromolekulare Chemie. Macromolecular Symposia. 1992, 60(1), 267–277. DOI: 10.1002/masy.19920600124.

[9] Zhang, X.; Tang, X.; Bowen, K. Photoelectron Spectroscopic Study of the Ethyl Cyanoacrylate Anion. Chem. Phys. Lett. 2013, 582, 21–23. DOI: 10.1016/j.cplett.2013.07.041.

[10] Stoyanov, P.; Akhter, S.; White, J. M. XPS Study of Metal/polymer Interaction: Evaporated Aluminum on Polyvinyl Alcohol Polymer. Surf. Interface Anal. 1990, 15, 509–515. DOI: 10.1002/sia.740150903.

[11] Duguet, T.; Gavriilides, A.; Esvan, J.; Mineva, T.; Lacaze-Dufaure, C. DFT Simulation of XPS Reveals Cu/Epoxy Polymer Interfacial Bonding. J. Phys. Chem. C. 2019, 123, 30917–30925. DOI: 10.1021/acs.jpcc.9b07772.

[12] Friedrich, J. F.; Koprinarow, I.; Giebler, R.; Lippitz, A.; Unger, W. E. S. Reactions and Intermediates at the Metal-Polymer Interface as Observed by XPS and NEXAFS Spectroscopy. J. Adhes. 1999, 71, 297–321. DOI: 10.1080/00218469908014853.

[13] DeKoven, B. M.; Hagans, P. L. XPS Studies of Metal/polymer Interfaces — Thin Films of Al on Polycrylic Acid and Polyethylene. Appl. Surf. Sci. 1986, 27, 199–213. DOI: 10.1016/0169-4332(86)90107-8.

[14] Possart, W.; Schlett, V. XPS of the Interphase between PMMA and Metals. A Study of Degradation and Interaction. J. Adhes. 1995, 48, 25–46. DOI: 10.1080/00218469508028152.

[15] Possart, W.; Dieckhoff, S. Adhesion Mechanisms in a Cyanurate Prepolymer on Silicon and on Aluminium. Int. J. Adhes. Adhes. 1999, 19, 425–434. DOI: 10.1016/S0143-7496(99)00005-6.

[16] Kusaka, I.; Suetaka, W. Infrared Spectrum of α-cyanoacrylate Adhesive in the First Monolayer on a Bulk Aluminum Surface. Spectrochim. Acta Part A. 1980, 36, 647–648. DOI: 10.1016/0584-8539(80)80022-5.
[17] Reynolds, S.; Oxley, D. P.; Pritchard, R. G. An Adhesive Study by Electron Tunnelling: Ethyl α-cyanoacrylate Adsorbed on an Oxidized Aluminium Surface. *Spectrochim. Acta Part A.* 1982, 38, 103–111. DOI: 10.1016/0584-8539(82)80183-9.

[18] Klarhöfer, L.; Roos, B.; Viöl, W.; Höfft, O.; Dieckhoff, S.; Kempter, V.; Maus-Friedrichs, W. Valence Band Spectroscopy on Lignin. *Holzforschung.* 2008, 62. DOI: 10.1515/HF.2008.116.

[19] Krischok, S.; Höfft, O.; Günster, J.; Stultz, J.; Goodman, D.; Kempter, V. H2O Interaction with Bare and Li-precovered TiO2: Studies with Electron Spectroscopies (MIES and UPS (HeI and II)). *Surf. Sci.* 2001, 495, 8–18. DOI: 10.1016/S0039-6028(01)01570-9.

[20] López, G. P.; Castner, D. G.; Ratner, B. D. XPS O 1s Binding Energies for Polymers Containing Hydroxyl, Ether, Ketone and Ester Groups. *Surf. Interface Anal.* 1991, 17(5), 267–272. DOI: 10.1002/SIA.740170508.

[21] Wu, C. R.; Salaneck, W. R.; Ritsko, J. J.; Bredas, J.-L. X-ray Photoelectron Spectroscopy of Polyacrylonitrile. *Synth. Met.* 1986, 16, 147–159. DOI: 10.1016/0379-6779(86)90107-4.

[22] Thøgersen, A.; Selj, J. H.; Marstein, E. S. Oxidation Effects on Graded Porous Silicon Anti-reflection Coatings. *J. Electrochem. Soc.* 2012, 159, D276–D281. DOI: 10.1149/2.jes113659.

[23] Vorotilov, K. A.; Petrovsky, V. I.; Vasiljev, V. A. Effect of Processing Temperature during Spin-on Application on the Properties of Sol-gel Silica Films. *J. Sol-Gel Sci. Technol.* 1994, 2, 559–562. DOI: 10.1007/BF00486309.