New materials equipped with functional surface features via novel composite coatings deposited using atmospheric PECVD
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A. Herrmann[1], A. Dohse[1], J. Köther[2], Y. Erguen[1], M. Thomas[1]

[1]*Fraunhofer Institute for Surface Engineering and Thin Films IST, Braunschweig, Germany*
[2]*VTT Verschleißteiltechnik GmbH, Langenhagen, Germnay*

Abstract: In this work, a new type of anti-sticking atmospheric PECVD coatings based on composite materials is presented. The coatings produced using process gases with two different silicon-containing precursors feature a good adhesion to the substrate material and at the same time an excellent anti-sticking behaviour to various polymers. Such coatings can be deposited on lamination plates where the coatings can potentially help to realize a better structure resolution and make possible the use of new lamination polymers.

Keywords: DBD, atmospheric pressure, anti-sticking, plasma-polymerized coatings, lamination.

1. Introduction

In the field of lamination plates as they are presently used, for instance, in the production of documents such as passports, driving licenses, national ID's and bank cards with integrated features market demands for finer structures is increasing. These will allow to implement more features and to access new application fields.

Currently, structures with dimensions of a thickness in the nm range and widths in µm desired by the market cannot be produced due to too high adhesion between the substrate and lamination tool which leads to parts of the polymer sticking to the metal plate after the lamination process. Thus, it can be expected that a suitable anti-sticking coating on the surface of the lamination plates solves these problems. In addition, it paves the way to the use of materials such as PET-G and PU.

2. Experimental

The coatings were deposited using a dielectric barrier discharge (DBD). The set-up, which is in principle shown in the scheme in **Fig. 1**, was modified to allow the deposition of coatings from a process gas containing a mixture of several precursors, or rather a deposition of a nanolaminate in one step.

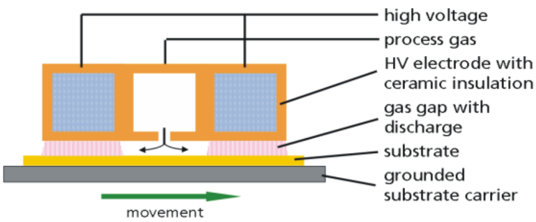

Fig. 1. Principle scheme of the set-up used in the PECVD coating experiments [1]

The properties of the coatings deposited on the lamination plates and a possible unwanted transfer to the laminated foil were investigated using several analytical methods.

For characterising the hydrophobicity contact angle measurements (Dataphysics Instruments GmbH, Typ OCA 20L) were used. The advancing water contact angle (CA) was measured using a dosing rate of 0.06 µl/s and an elliptical fit for the contour of the drop.

The samples were laminated with a thermoplastic polyurethane foil (TPU) by a thermo compression bonding system (developed by the Fraunhofer IST) at 175°C and a pressure of 600 N/cm^2 for 90 s.

Afterwards the samples were tested for release properties by a tape test at a 90° angle on a universal testing machine and then pulled off the substrate at a velocity of 120 mm/min.

ATR-FTIR measurements on metal plates and laminated foils were carried out with a "Nicolet IS10" FTIR spectrometer from Thermo Scientific with a single reflection diamond ATR crystal in order to investigate a possible transfer of the coating to the lamination foil.

The thickness of the deposited layers was measured by spectral ellipsometry on Si wafers as substrates using a spectral ellipsometer "SE 850 DUV" from Sentech Instruments.

3. Results and Discussion

In a first step, potentially suitable precursors were selected. These included two silicon-containing compounds, one known to produce adhesion-promoting character and the other one known to produce anti-sticking behaviour. From (partially mixtures of) these precursors three different types of composite coatings were deposited on the lamination plates (**Fig. 2**).

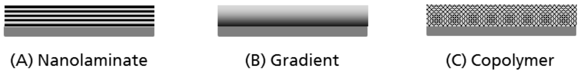

Fig. 2. Types of composited coatings.

1. Nanolaminate: this coating consists of two different single-layers of only a few nm thickness, which are alternatingly deposited. Bottom layer is the adhesion-promoting layer, top layer is the anti-sticking layer.

2. Gradient: In the gradient coating, the two precursors continuously change their concentrations over the coating thickness in order to achieve a smooth transition from the adhesion-promoting to the anti-sticking properties.

3. Copolymer: Here, both precursors were mixed before entering the plasma zone and are deposited simultaneously on the substrate and form a close network.

Figure 3 shows the results of the contact angle measurement that provide information on the anti-sticking behaviour of the deposited coatings. It can be seen that two types of coatings, namely the nanolaminate and the gradient, led to a hydrophobic surface. Contact angles of about 110° to 115° were generated. The copolymer coating deposited showed contact angles of about 80° and thus was even slightly less hydrophilic than the uncoated reference. The copolymer based composite therefore seemed an unlikely candidate to generate the desired anti-sticking effect.

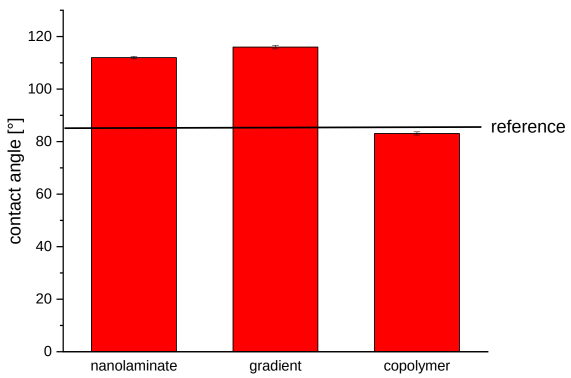

Fig. 3. Contact angle measurements on coated plates.

The following **Figure 4** shows subtracted ATR-FTIR-spectra obtained by measuring the polymeric foils after the lamination and the subsequent peel test. After the measurement reference spectra were subtracted from the spectra recorded and peak areas were determined. Vibration bands found in the wavenumber range of 1000 – 1200 cm^{-1} are assigned to the presence of Si-O bonds in the plasma coatings. A comparison of the peak areas of the three different composites revealed that in case of the copolymer a significant amount of the coating was transferred to the polymer during the lamination process. In contrast, in the case of the gradient and nanolaminate coating spectra showed no vibrational bands typical for the Si-O-bond could be identified which is taken as evidence that there is no coating transfer. It is concluded from these results that in the case of the gradient and nanolaminate coating the adhesion within the coating and between coating and lamination plate seems to be high enough for a lamination process.

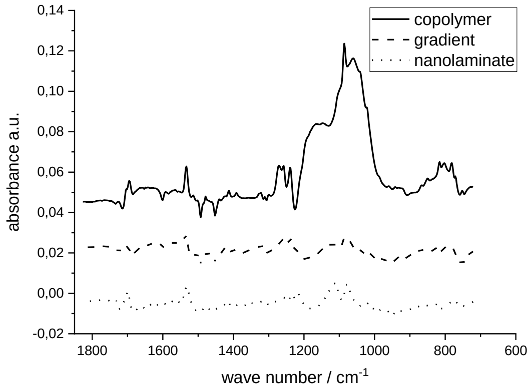

Fig. 4. Subtracted IR-spectra of laminated polymer foils after peel test.

These observations fit quite well to the results of the subsequent peel tests performed, results of which are shown in **Fig. 5**. According to this the anti-sticking property of the copolymer was very weak. It seemed to adhere strongly to both sides, to the lamination plate as well as to the laminated foil. During the peel test, the coating shows a coherent failure which is attributed to the strong adhesion to both interfaces. Taking into account also those results obtained by IR and contact angle measurements it can be summarized that the copolymer does not combine anti-sticking and adherent properties, but rather leads to a coating with a very strong adhesion to both, metal and polymer, interface.

The nanolaminate showed much better results than the copolymer. Here, the peel forces were only one third of those measured in the case of the copolymer yet in comparison with the non-coated reference no improvement was observed.

The best results with respect to the desired anti-sticking property were obtained with the gradient material. Here, the peel force is a 100 times greater than in the case of the reference material. The lamination foil delaminates and more or less “drops off” the lamination plate.

All of these results were obtained with a thermoplastic polyurethane as lamination foil. Currently, it is not possible separate this polymer from the lamination plate in industrial application.

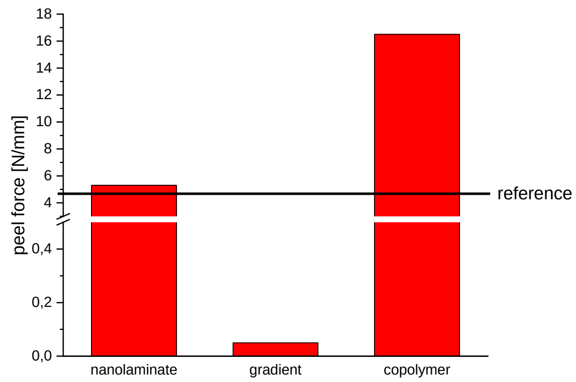

Fig. 5. Peel forces as a function of the different types of coatings.

After selection of a suitable type of composite, the influence of the coating thickness on the peel force was investigated. Figure 6 shows the peel force as a function of the path length of the lamination plate for three different substrate velocities (1mm/s ≙ 180 nm; 2 mm/s ≙ 60 nm; 4 mm/s ≙ 17 nm). Coating thicknesses thinner than 60 nm led to a decrease of the peel force and to a reduction of the anti-sticking effect. It is conceivable that this observed reduction is due to reduced long-term stability of the thinner layers.

It is also striking that at the end of the lamination plate the peel forces are increasing. This can be justified by edge effects which may appear at the edges of each lamination plate during the plasma coating process which is able to lead slightly inhomogeneous coatings.

Best results were achieved with the thickest coating. The curve shape (black line) is quite flat, so it can be assumed that the coating was deposited very homogeneous.

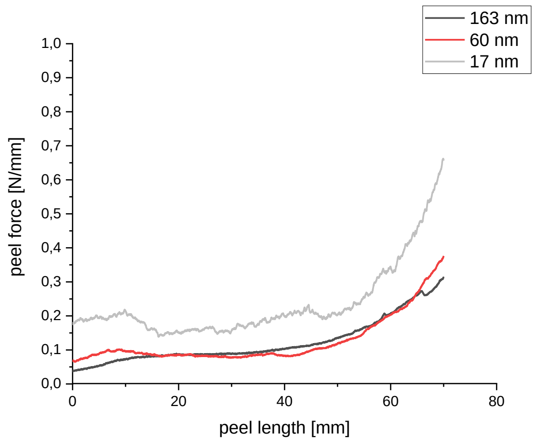

Fig. 6. Peel forces as a function of the thickness of the anti-sticking coating.

4. Conclusion and outlook

In this work we have demonstrated the atmospheric pressure PECVD deposition of novel composite based anti-sticking coatings on metals in order to improve the structure resolution of lamination processes using thermoplastic polyurethanes (TPU).

Best results were achieved with the gradient coating, where the composition of the coating continuously changes over the thickness of the coating. With this gradient coating, a stable coating showing good adhesion to the lamination plate and anti-sticking properties in the industrially desired order of magnitude. In the future the work will be focussed on optimization the process for further polymers to broaden the range of materials using for lamination for documents such as passports, driving licenses, national ID's and bank cards.

5. Acknowledgements

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6. References

[1] C.-P. Klages, Vakuum in Forschung und Praxis 14 (2002).