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Roll-to-roll structuring and PECVD coating of polymer foils

Enhancement of hydrophobicity for various applications

Jakob Barz, Georg Umlauf

1 Introduction

In many industrial and daily-use applications, plasma technology plays a key role when it comes to providing tailored surface properties on different materials in a cost-efficient way [1]. Plasmas can be used for cleaning, activating, functionalizing and coating. To achieve these different aims, a huge variety of gases or vapors can be used in various types of plasma plants suitable for atmospheric and/or low-pressure plasmas, and the plasma process parameters can be varied. When it comes to coating processes, ultrathin films can de directly deposited from the gas phase from monomers being activated in the plasma. Alternatively, plasma processes can be also used for chemically activating the material to be coated prior to using a wet-chemical coating step (bath or spray deposition). This technology can be combined with other techniques like hot-embossing of polymers, which allow to alter the surface topography.

This article deals with the combination of these versatile techniques in roll-to-roll systems (R2R) and the properties which are achieved, and compared to the ones obtained in batch processes. From this combination, advanced tailored surfaces are resulting

2 Technologies

2.1 Plasma technology and PECVD coatings

Plasma deposition in closed chambers, in particular at low pressures in the range of 100 Pa and below, allows to deposit uniform plasma polymer coatings from monomolecular layers up to the micrometer range with high purity. In the process, the chamber is first evacuated to the base pressure of the system, typically in the range of 5 Pa and below. Then, the process gas is introduced. By starting the plasma, several processes start simultaneously. Besides partial electronic excitation and ionization of the process gas, molecular bonds are broken in the gas phase in such chemical radicals are produced, which can undergo subsequent chemical reactions. At the same time, chemical bonds of the to-be-coated material (substrate) are cleaved and act as anchor side for the molecular fragments impacting from the gas phase. The overall process is referred to as PECVD – plasma-enhanced chemical vapor deposition.

FIGURE 1: **Pink V340-GKM plasma chamber for R2R coating.**

Besides the process gas which provides the reactants, the proportions of gas-phase and surface processes play a major role on the resulting coating properties [2]. They do not only depend on the gas composition, pressure, and plasma power, but in particular on the plasma source. Typically, alternating voltage sources are used in R2R, starting in the kHz range (low-frequency plasma) and reaching up via the MHz range (referred to as radio-frequency plasma) to the microwave plasma regime in the GHz range. As a rule of

SUMMARY

In the innovation field “Functional Surfaces and Materials” at the Fraunhofer IGB, research is being carried out to tailor the surface properties of PU foils and other materials via roll-to-roll processes. The goal is to save considerable costs by applying a unique and resource-saving structures and coatings to self-adhesive, transparent and erosion-resistant PU foils to equip various technical devices with water and ice repellency. We are now able to obtain such surfaces in two separate roll-to-roll processes using low-pressure plasma (pressure p < 100 Pa) in combination with a microstructuring process. Through structure and coating, the contact area and adhesion are minimized. Compared to an untreated reference surface, we are able to increase water contact angles from 76° to 157°. The structuring and coating of polymer foils make it therefore possible to open up new fields of application at lower cost than direct treatment of the various technical surfaces.

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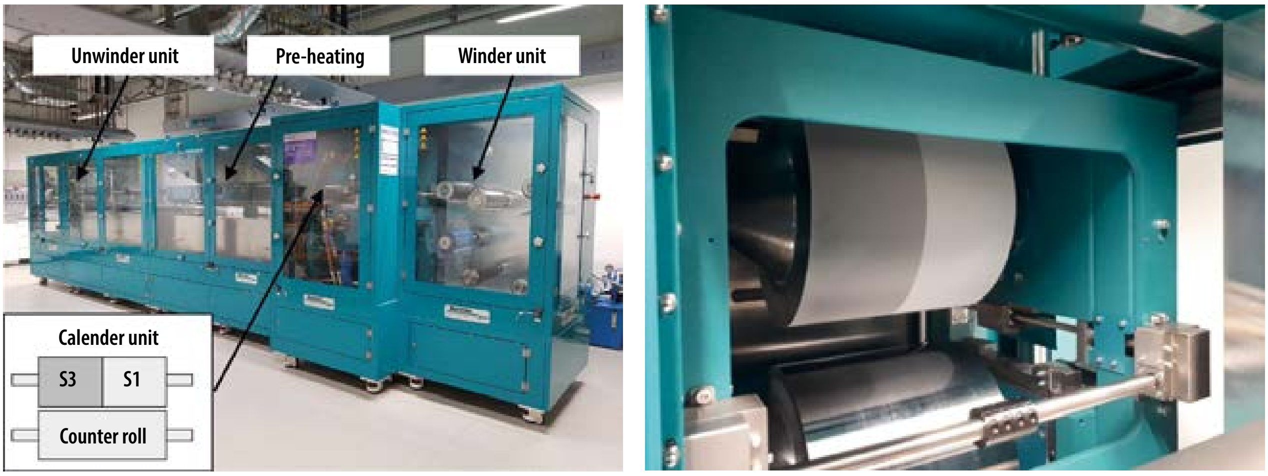

FIGURE 2: **Left: Total view of the plant with unwinder, pre-heating, calender and winder unit. Right: Detailed view into the calender unit with the two-part structured calender roll.**

thumb, increasing the frequency results shifts the amount of energy deployed from the substrate to the gas phase and therefore results in less surface-bond cleavage and higher fragmentation rates in the plasma.

2.2 Surface structuring

For surface structuring, mainly hot-embossing is used at the Fraunhofer IGB to structure the surface of thermoplasts through contact of foils with a stamp at elevated temperature and high pressure. Several parameters are decisive for the obtained result which are the temperature, the heating (approx. 80 °C) - and cooling profiles, and the process load (F > 100 kN). Obviously, the optimum parameters are depending on the polymer properties and are adapted in each case. Depending on the temperature and holding time at high pressure, different structure heights can be achieved in the foil. This is reflected in the static contact angles. The range of achievable structure heights is between 10 µm and 40 µm. In this case, the static contact angle of blank PU foil may increase up to 135° after a batch hot-embossing. In a further technology step, the structuring and plasma coating process is transferred to two R2R processes. A R2R process has to meet certain requirements which limit the possible process steps. For example, in batch processing, the foil is often preheated in the embossing unit at minimum pressure before applying full load to achieve surface structuring. But this is only possible to a very limited extend in R2R processes. Preheating with infrared of hot air is possible, but requires careful process control and should be avoided in particular on sensitive material or multi-component systems such as foils with additional adhesive layers. A second parameter which cannot be directly transferred to a continuous process is the holding time of the stamp. These considerations should already be taken into account during the early-stage development in lab batch-processes.

ZUSAMMENFASSUNG

Rolle-zu-Rolle-Strukturierung und PECVD-Beschichtung von Polymerfolien – Erhöhung der Hydrophobizität für verschiedene Anwendungen

Im Innovationsfeld „Funktionale Oberflächen und Materialien“ des Fraunhofer-Insituts für Grenzflächen- und Bioverfahrenstechnik IGB wird an der gezielten Oberflächenausrüstung in Rolle-zu-Rolle-Verfahren gearbeitet. Ein Schwerpunkt liegt dabei auf der Ausrüstung von Polyurethan- und anderen Folien. Ein Ziel ist, ressourcen- und kosteneffizient über spezielle Strukturierungs- und Beschichtungsverfahren wasser- und eisabweisend ausgerüstete PU-Folien herzustellen. Das Basismaterial ist dabei selbstklebend, transparent und erosionsstabil, und somit für viele Oberflächen zur Veredelung geeignet. Über zwei separate Rolle-zu-Rolle-Prozesse auf Basis eines Niederdruckplasmas (Druck p < 100 Pa) sowie eines Kalandrierungsverfahrens zur Mikrostrukturierung konnten bereits jetzt wichtige Teilerfolge einzelner Schritte und von Verfahrenskombinationen erzielt werden. Die Kombination aus Struktur und Oberflächenchemie ermöglicht es, die Kontaktfläche für Adhäsion zu minimieren. Auf diese Weise wird beispielsweise der Wasserkontaktwinkel von 76° auf rund 157° erhöht. Es eröffnen sich neue Anwendungsgebiete, da die Technologie auf kostengünstiges Folienmaterial übertragen werden kann und nicht mehr ganze Geräte- oder Maschinenoberflächen einzeln behandelt werden müssen.

3 Equipment

3.1 Plasma plants

For the development of coatings at the lab scale, small plasma batch reactors are used which are typically suitable for dimensions up to DIN-A3 formate. For the upscaling R2R deposition, two different reactors are available.

The reactor suitable for foils as well as woven and non-woven materials is a customized plasma chamber V340-GKM from PINK GmbH Thermosysteme, Wertheim, Germany (**Fig. 1**). It possesses a winding setup where both coils are placed inside the vacuum

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chamber. Two different plasma sources can be used: One of them is a cooled radio-frequency electrode system as depicted in **Fig. 1, right side.** The second source is a microwave-operated duo plasmaline setup from Muegge GmbH, Reichelsheim, Germany. This allows to use both types of plasma with high or low surface activation / low and high gas phase fragmentation rates, respectively.

The second R2R setup is a self-made low-pressure fiber treatment system. It operates air-to-air via several pressure stages. The fiber transport can be carried out by conventional winders which allows to account for different winding speeds etc.

3.2 Structuring

The multifunctional plant is a set of several elements for individual production of continuous material. The basic device is the SC24 from Coatema, Dormagen, Germany. The component needed for structuring is the calender unit with optional preheating by hot air (**Fig. 2, left**). The upper calender roll has a structure in the micrometer range, see **Fig. 2, right.** The adjustable counterpressure of the lower calender roll (without structure) allows the negative structure of the upper roll to be transferred to the foil. In addition, the rollers can be individually heated to achieve increased structure imaging. Another process parameter is the foil speed which can be up to 10 m/min.

Structure S1 creates cylindrical elevations on the foil surface with hemispherical toppings, whereas S3 creates hexagonal deepenings. Both structure dimensions are in the mid two-digit micrometer range. The structured calender roll has a width of 400 mm.

3.3 Combined system for plasma and wet chemistry

In addition to the plasma systems mentioned in 3.1, an additional plasma chamber with an volume of about 1 m^3 is available which can be operated at different pressures as well as in combination with wet chemistry. It is depicted in **Fig. 3.**

This reactor is suitable for screening purposes, e.g. plasma activation and subsequent spray-deposition of reactive chemicals. It provides a closed environment not only for the usage as low-pressure system, but also to control the gas atmosphere (e.g. inertness) at elevated pressures and, if necessary, keep potentially hazardous wet-chemicals in a closed compartment.

3.4 Surface and interface analysis

For tailored surfaces, process characterization is essential. A wide range of analytical equipment is available in-house for this surface and interface analysis.

Functional testing
The most straight-forward testing is functional testing. It depends on the application of the coating. For surfaces requiring a certain wettability, either test inks are used or contact-angle measurements are performed. The latter method ranges from simple sessile-drop measurements over dynamic measurements to the complete assessment of the free surface energy (DIN EN ISO 19403). More specialized tests are for example tests for the ice adhesion [3] for anti-ice applications or assessment of photocatalytic activity for self-cleaning surfaces by discoloration or direct measurement of radicals [4].

Chemical characterization commonly used during coating development
A cost-efficient broad-spread method is Fourier-transform infrared spectroscopy (FTIR). Add-ons like reflection units for grazing-incidence spectroscopy allow to characterize ultrathin films on IR reflective materials. As an example, fluorocarbon plasma polymers provide signals already at thicknesses of some tens of nanometers when deposited on Gold or Aluminum reflectors. More suitable for coatings on foils is attenuated total reflection (FTIR-ATR). Due to the penetration depth of about 500 nm to several microns, coatings should be thick enough to provide clear separation from the substrate signal.

Electron-spectroscopy is a much more sophisticated way of surface characterization commonly carried out in specialized labs. Depending on the method, electrons leaving the substrate are analyzed regarding amount and energy. In case of XPS, electrons are released via the photo effect. They provide both information on the elemental composition and the binding states of the uppermost five to ten nanometers. UPS, ultraviolet photoelectron spectroscopy, provides information about the valence bands in the same range. Auger electron spectroscopy provides a higher lateral resolution and is more surface sensitive than XPS. It provides mainly the elemental composition of the surface.

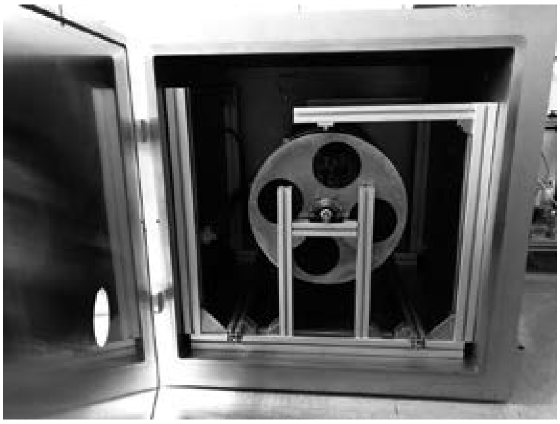

FIGURE 3: Setup of the multi-operational treatment chamber.

4 Process examples and achieved properties

The following passages present some process examples and resulting surface properties. As major benchmark for easy comparison, water contact angles are given. For better readability, the standard error is not always given. The typical standard error is ±2°.

4.1 Plasma polymers

Fluorocarbon plasma polymer coatings
Fluorcarbon plasma polymer coatings were applied to a PU foil (PU 63630, CMC Klebetechnik, Frankenthal, Germany or PU 4932, Gerlinger Industries GmbH, Schwarzhammermühle, Germany) as used in previous experiments [5] for ice- and water repellent properties in a R2R process. The data shown in **Fig. 1** result from a process carried out in the PINK V340-GKM plasma chamber at three different foil velocities and two different gas flows. All other parameters were kept constant (300 W r.f., 20 Pa pressure). The pressure was controlled via a throttle valve.

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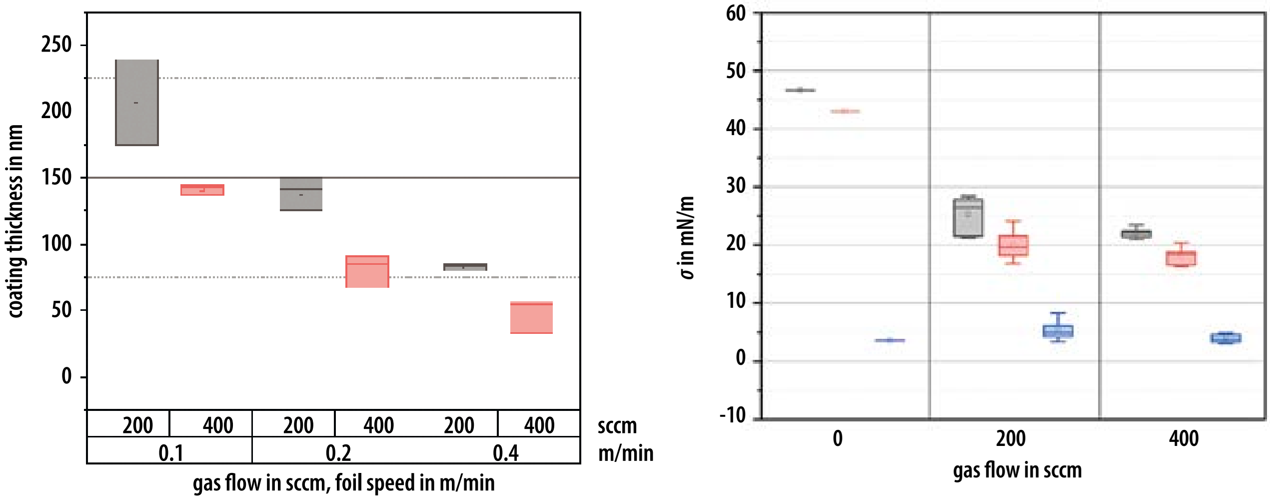

FIGURE 4: Left: coating thickness at different foil speeds (0.1, 0.2, and 0.4 m/min) and two different gas flows (200 and 400 sccm). Right: total (grey), disperse (red) and polar (blue) contributions to the surface free energy *σ*. Data at 0 represents the respective values of the uncoated reference.

Foil Material	Structure and coating	Advancing contact angle
PU 63630	S1	105
PU 63630	S1 + Fluorocarbon	119
PU 63630	S3	103
PU 63630	S3 + Fluorocarbon	118
PU 4932	S1	124
PU 4932	S1 + Fluorocarbon	133
PU 4932	S3	133
PU 4932	S3 + Fluorocarbon	157

TABLE 1: Effect of structuring and coating on two different types of PU foils used for antiadhesive applications.

The left part of **Fig. 4** shows the influence of foil speed on the coating thickness. The faster the foil moves through the plasma zone, the lower the coating thickness. It should be mentioned that by doubling the foil speed, the resulting coating thickness is more slightly more than 50 % of the previous value. Further, doubling the monomer flow of C_4F_8 results in a lower coating thickness. One reason for this behavior is the ratio of the electrical energy available per molecule which is responsible for the radical formation by fragmentation of the monomer. A second reason may be the composition of the gas phase during the process, which is not only composed of the monomer feed gas, but also form outgasing of the foils. The ongoing gas-phase chemistry induced by such contaminations may be responsible for shifting of the fluorine-to-carbon ratio, which is responsible for the deposition rates in the particular case of fluorocarbon plasmas [6].

For the applications, the wettability is more important than the coating thickness. The box plot in **Fig. 4, right**, shows that mainly the disperse free surface energy is significantly reduced by the plasma coating. In this case, the reduction is slightly more pronounced at the higher gas flow (400 sccm). The reason is the higher purity of the gas phase composition and the higher content of Fluorine in the coatings. For comparison, PTFE surfaces also possess values of around 20 mN/m. With water, θ_A =118° and θ_R = 77° were measured as advancing and receding contact angles, respectively. In an A3 reactor, using similar power densities, θ_A = 115° and θ_R = 105° were achieved. The difference between the receding contact angles can be further optimized.

Silicone-like plasma polymer coatings

The silicone-like coatings were deposited on PU foils in order to achieve hydro- and/or icephobic properties. As precursor for plasma polymerization, Hexamethyldisiloxane (HMDSO) was used. Such coatings were already investigated in more detail for the target properties in the past [7]. For the transfer from batch to R2R coating, the main focus was on the coating thickness and the water contact angle as a function of the foil speed as well. In the R2R process, an HMDSO flow of 4 sccm at a power of 350 W was used. The foil speed was adjusted to ensure a sufficient film thickness of 200 nm. The foil PU 63630 already showed hydrophilic character in its initial state (advancing angle < 80°). For PU 4932, the initial angle without coating is θ_A = 87°. After plasma coating with HMDSO, all samples show a similar advancing angle of θ_A = 114°. The receding angles increase from θ_R = 58° in the initial condition, to θ_R = 73° for coated foils.

4.2 Combined structuring and coating processes

Embossing and subsequent PECVD coating

One way of polymer processing to achieve repellent properties is to first structure the polymer surface and to coat with an ultrathin hydrophobic plasma polymer afterwards.

In **Table 1**, the results of contact-angle measurements on structured and coated PU foils are listed. Two different structures and two different types of polymer foil were used. In addition, the effect of a plasma-polymer top coating is illustrated. Looking at the first polymer, PU 63630, the contact angle is similar for both structures S1 and S3, and can be increased through a plasma coating by about 15°. The second material, PU 4932, behaves quite different during the structuring process. Here, the contact angles differ already by 9° on uncoated material. Through an additional topcoat, the differences become even more pronounced. As a maximum in this set of experiments, an advancing contact angle of 157° was achieved. The receding contact angle in this case was

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152°, therefore resulting in superhydrophobic surface properties and very easy roll-off of water droplets.

PECVD coating and subsequent embossing

In some combinations of foil material and the desired structure dimensions, the foil tend to stick to the calender unit during the structuring process. This has a significant influence on the structure result and consequently, on target properties like the water contact angles and the ice repellency. To overcome this issue, the process can be adapted by first coating the foil with e.g. a silicone-like plasma-polymer layer and subsequent structuring. As an example, a structuring process with structure S3 was carried out on PU 63630. In this case, the evaluation of the contact angles showed an increase from 76° (without structure or coating) to 111° after a HMDSO plasma coating and a subsequent structuring. For comparison, in a lab batch process with an initial HMDSO coating and subsequent structuring, a contact angle of 104° was measured. Using the identical sequence for manufacturing (first HMDSO coating, second structuring), but adding a CF topcoating, enabled a contact angle of 118°. The last result is identical to the one obtained for the same structure and foil without HMDSO coating prior to the embossing process. From the view of processability, the prior plasma coating has the advantage of the structuring process running more stably.

5 Conclusion

The upscaling from batch to R2R processes may bear some challenges. In lab batch processes, it is for example easily possible to carry out hot embossing of polymers by more or less sophisticated temperature- and pressure profiles. However, when it comes to a R2R process, such steps are either difficult/expensive to carry out and have to be limited to a minimum. It is therefore important to think of these upscaling steps already during the early steps of development in the batch scale and to focus on the most promising process routes. In such a way it could be shown that a batch-process for structured superhydrophobic surfaces could be successfully transferred to a R2R process. As a result of the increased variation possibilities of the two separate R2R processes for structuring and coating, we are able to produce individual larger quantities of R2R foils compared to a batch process. Due to process optimization, it is now possible to quickly adapt the water-repellent finish to specific requirement profiles.

In order to take even greater account of environmental considerations, currently in-depth research on silicone-type coatings with consistent water-repellent properties is carried out for applications, which do not require extreme hydrophobicity and omnirepellency. Further, the the material portfolio of foils that can be used is extended.

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