

Practical Aspects of Plasma Treatment for Thin Film Adhesion on Polymer Substrates

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Contributed Original Article

Introduction

Plasma treatment of polymers has been the subject of numerous publications. Several excellent resources are referenced here and the *SVC Technical Conference Proceedings* have many more. Even so, there may be room for some practical tips and tricks and that is the goal of this article.

If there is a take away message it is that plasma treatment (PT) of polymers is a tuned process and should be approached with as much care and science as a thin film coating process. Without this approach, PT often gives poor results and is abandoned or not optimized. In fact, the most common failure of PT is over treatment. When a simple, step-by-step process is used, the optimum treatment can be determined and monitored to insure the required performance is achieved and maintained.

Often the deposition process itself provides sufficient UV energy or particle flux to the polymer for sufficient thin film adhesion. In some cases adhesion can only be achieved with a separate plasma treatment process. An advantage of a dedicated plasma treatment step is the ability to optimize adhesion independent of deposition.

Plasma Treatment Considerations

Plasma treatment in the context of this article is done *in situ* prior to the vacuum deposition process. In implementing a plasma treatment process, primary considerations include the speed of the substrate, the substrate material and the plasma treatment source. The speed the substrate moves past the PT source and the particle flux emitted by the source result in a treatment “dose” rate and total dose on the substrate. As will be seen below, this is a key concept for optimizing adhesion. Though the substrate speeds are as varied as applications, PT processes can be grouped into two speed ranges: High speed PT associated with thermal and e-beam evaporation processes (in the range of 6-10m/s) and low speed for sputtering and PECVD processes (1-10m/min). With high speed applications, the challenge can be to apply sufficient dose to reach optimized treatment. With low speed applications the opposite is often the case and too high a dose results in over treatment.

Of course the polymer substrate itself plays a large role in determining both the PT process settings and the potential results. The chemical makeup of the polymer and the polymer manufacturing process result in unique surface conditions. To dive into specific polymer details is beyond the scope of this article. The approach to PT process optimization presented here is universal to all polymers. There are many references available for specific polymers and research on your substrate material is certainly advised.[1,2]

A number of plasma sources have been developed and implemented for plasma treating polymers.[3, 4, 5, 6] There is no one source that is necessarily better than the rest and people have their favorites. Any way it is formed, plasma in contact with the polymer substrate effectively bombards the surface with a rich mix of photons, electrons, ions and radical compounds and these particles interact with the surface to remove water vapor and oils and create bond sites for the depositing film. That said, here are questions to consider in selecting a plasma source:

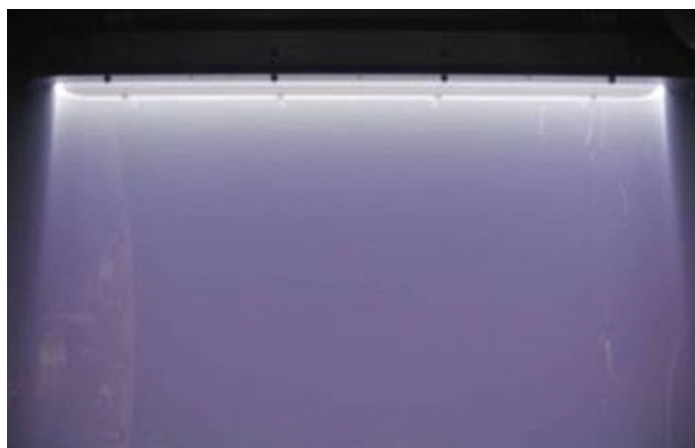


Figure 1. A linear, anode layer ion source in operation

- Is the dose rate generated by the plasma source relative to the substrate speed sufficient to optimize surface treatment?
- What are the pressure and gas flow requirements of the source? In the case of a DC glow bar, the pressure around the bar must be relatively high (100mTorr). At a minimum this dictates where the source must be installed in the coater.
- How physically big is the source? Can it fit in your tool and how will it affect threading (in the case of web treatment)?

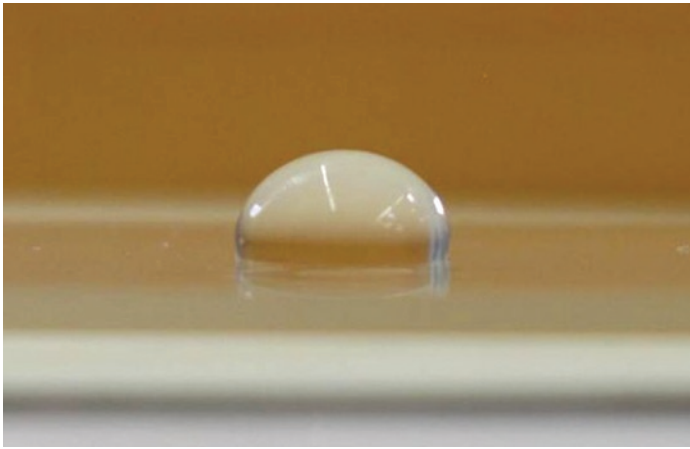
Other important source selection considerations are initial cost, maintenance requirements and operation stability over time. Figure 1 shows an anode layer ion source in operation. These sources are one effective option for plasma treatment.

Plasma Treatment Optimization

Optimizing adhesion between a polymer and thin film is a two step process. First, the effect of plasma treatment on surface tension is determined on the uncoated substrate. Then the thin film is deposited and adhesion is directly measured and optimized. It is important to take the steps in order.

Before starting you will need some simple, low cost materials. To measure surface tension you will need either dyne pens (Diversified Enterprises (www.accudynetest.com)) or a syringe and purified water. For adhesion have 3M type 810 scotch tape on hand.

A water drops behavior on the substrate surface is very instructive. If the water spreads out over the surface this shows the water molecules are more attracted to the surface than to itself. The attractive quality of a surface is determined by its surface tension measured in units of dyne/cm. Pure water has a surface tension of 73 dyne/cm. If the water forms a spherical drop, this shows the substrate surface tension is less than that of the water, i.e. the water molecules would rather stick together than attach to the polymer surface molecules. Figure 2 shows water drops on both untreated and plasma treated surface. (Mercury has a surface tension of 470 dyne/cm so it beads up on just about everything.) The dyne pens are useful to get a more absolute measurement of surface tension. The pens come in steps of 5 from 30 to 60 dyne/cm.



Water drop on an untreated, low energy surface

Figure 2. Surface tension effect of plasma treatment.



Water drop on a plasma treated surface

Step 1 - Develop Plot of Plasma Treatment Dose vs. Surface Tension

The surface tension plot in Figure 3 is typical for most polymers when treated with plasma. As the treatment dose increases, the surface tension increases to a point and then levels off. The higher the tension, the better the thin film will stick provided the surface is not degraded. The danger in relying only on surface tension measurement to determine the correct treatment dose is the test gives no indication of polymer surface integrity. While plasma effectively breaks bonds and creates bond sites for a thin film, excessive treatment breaks polymer chains to the point of creating powder on the surface. When measuring the wetting property of the surface, over treatment is not apparent. To the wetting agent (water or dyne pen liquid), highly attractive bonds on dense

polymer or powder are equal.

The first step then is to create a surface tension plot for your substrate and operating conditions. Start by measuring the untreated substrate. It is highly advised to have an untreated control along (next to) each treated sample. This will clearly define the treatment results and avoid false positives. As the amount of treatment is increased and samples begin to have the same, high surface tension, then the dose is too high and you are on the flat part of the curve. It is highly likely you are over treating. Lower the dose and get a couple data points off the plateau. This test is performed without depositing the thin film (you are only measuring the bare polymer surface).

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Plasma Treatment

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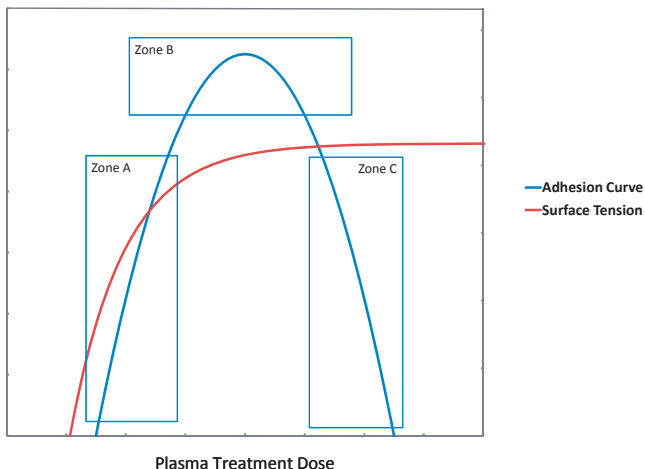


Figure 3. Graph of adhesion and surface tension vs. plasma treatment dose

Step 2 - Develop Plot of Plasma Treatment Dose vs. Thin Film Adhesion

With the surface tension plot completed you are ready to make films - and optimize adhesion. Referring to Figure 3, the plot of dose vs. adhesion has been grouped into three zones: Zone A - Under Treatment, Zone B - Optimum Treatment and Zone C - Over Treatment. Here is what is happening to the polymer surface in each zone:

Zone A: Active sites are being created on the web surface and water vapor and other contaminants are being removed. Adhesion improves and surface tension increases (water contact angle drops).

Zone B: The optimal condition is reached for a particular polymer. Surface water vapor and low molecular weight compounds are removed to a satisfactory degree without excessive polymer chain scission. The surface polymer chains remain sufficiently intact to maintain bond strength between the surface and bulk material.

Zone C: This is the over treatment zone. Here the long polymer chains responsible for the strength at the polymer surface have been excessively broken. While the surface tension is high, thin film adhesion will be poor. Really the thin film interface is not the problem. The surface polymer is no longer adhering to the underlying bulk material.

Similar to Step 1, the key in Step 2 is to obtain sufficient data points to plot the full curve. As a starting point, begin at the knee of the surface tension plot. Now you can see the importance of the surface tension plot. Without it, data points for adhesion can be taken on each side of the adhesion curve (Zones A and C) with the same results. With the surface tension plot you have information on which zone the data point resides and where to go with the test.

Final Notes

- Adhesion measurement by tape test is standardized in ASTM D3359 (www.astm.gov.) Often it is not necessary to cut grids on the sample as quickly pulling well adhered tape from the surface is sufficient to determine adhesion quality. Either way the test and required results are typically dictated by the end customer.
- Humidity is the bane of thin films. An initially adhered thin film often falls off after a few days at 85°C/85RH. As this is well known, heat/humidity tests are commonly specified. To get faster

feedback on progress, boiling the sample in water for 1-2 hours often predicts performance of a multi-day environmental chamber test. In the end though, the final product must endure an extended environmental chamber test.

- Keep an eye on your base pressure. A changing base pressure can affect your plasma treatment results. Given that the residual gas is likely water vapor, this oxygen source can shift your treatment process.

Further Plasma Treatment Information

A large number of publications are available on the subject of plasma treatment. The author has found several highly informative: Liston et al⁷ gives a detailed, scientific look at the chemistry of plasma treatment with special attention paid to the polymer-film interface. Kittler and Diffendaffer⁸ and Rank et al⁹, review the hardware associated with plasma treatment and offer useful tips. Egitto and Matienzo¹⁰ give an excellent overview of surface effects and treatment techniques. Burger et al is another useful publication.¹¹

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John Madocks is the President of General Plasma, Inc., a manufacturing company building vacuum deposition systems and components. John received a B.S. in Mechanical Engineering in 1981 from Cal Poly in San Luis Obispo and has worked in the vacuum industry his entire career – mostly in large area thin film coating. In 1997 John started his own consulting company that today is General Plasma. John has 13 US patents and 12 more in the application stage and has many industry presentations and publications to his credit.



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