Long Lasting Surface Activation of Polymer Webs

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ABSTRACT

Surface activation of polymer films to modify surface properties is widely practiced to enhance wettability, printability and adhesion properties of these films. Sigma Technologies has been actively pursuing the area of long-lasting activation of polymer films using various techniques including plasma technology. Atmospheric glow discharge plasma technology has been a recent addition towardsthese efforts. Plasma activation using a variety of precursors has been investigated for long lasting functionilization of various substrates. Latest developments in the area of surface activation of polymer films will be presented.

INTRODUCTION

Polymers of various chemistry have become most common in our life, many of todays amenities certainly were not realizable without the use of one or more polymer materials. Although polymers are so common in every days living, the most commonly used like those out of the group of polyolefines inhibit a significant problem: As shown in Table 1 the intrinsic surface energy of these materials is rather low, and processes like bonding, printing or coating present a rather difficult challenge.

Polymer	Surface Tension of Homopolymer [dynes/cm^2]
Polyethylene (PE)	31
Polypropylene (PP)	32
Polyisobutylene	27
Polystyrene	33
Polytetraflourethylene	19

Table 1: Surface Energy of various Homopolymers

Different approaches are possible to alter the surfaces of such materials in order to allow the above processes:

Mechanical: Roughening polymer surfaces mechanically by grinding, brushing, blasting or similar methods creates enough sites were glue or paint can physically grab on. The cutting action on the surface during such a treatment also may cut polymer chains, creating open or dangling bonds exposed at the surface. This allows for improved chemical bonding on the surface. There are several disadvantages to mechanical treatment: Increased surface roughness in the macro scale is not always wanted, and the treatment sometimes simply is too expensive to apply.

Chemical: Treating polymer surfaces with chemicals can alter the surface chemistry to improve the surface energy by providing active chemical bonds or groups on the polymer surface. The highly inert behavior of most polymers however often requires chemicals, which are problematic in terms of handling and environment.

Treatment with Ionized Gases: The most common method to increase surface energy on polymer films is the use of ionized gases impinging on the polymer surface. Four major effects take place on the surface of the polymer film during a treatment with ionized gases:

- Electron Bombardment: Electrons, generated in the electric field of a plasma, hit the surface with a wide distribution of energy and speed. This will lead to chain scission in the upper layer of the polymer, but can also create crosslinking, therefore in reinforcing of the polymer material.
- Ion Bombardment: Ions, generated either in the electric field of a plasma or during the chemical reaction in a flame, hit the surface of the polymer surface with a distribution of different energy and speed. This leads to etching and sputtering, therefore cleaning of the surface substrate. Effective removal of low molecular weight structures can be performed.

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- Excitation of Gases: Ionization of Gases also means the presence of many excited species in the gas. By using the right mixture of gases those excited species react with the polymer surface to create functional groups such as hydroxyl (-OH), carbonyl (-C=O) carboxyl (-COOH) or amino (NHx), which exhibit high polarity and change the base/acid interaction at the polymer surface.

While the function of plasma on polymer surfaces has been described in numerous publications (e.g. 1 – 3), it is also well known, that in most cases the surface treatment with ionized gases is not of lasting nature. On some polymers the surface treatment can last several weeks, while on others the effect of treatment disappears within days or hours. Major reasons for the decay of surface treatment is the recombination of active groups as well as the disappearance of such groups in the bulk material.

In the following the methods for treating polymer surfaces with ionized gases will be shortly described and compared. A new developed method to treat polymer surfaces at atmospheric pressure is presented, along with results showing that long lasting treatment of certain polymer surfaces is possible.

PLASMA TREATMENT OF POLYMER SURFACES

Commonly used methods used for the treatment of polymer films with ionized gases are

- Flame Treatment
- Corona Treatment
- Plasma Treatment in Vacuum
- Plasma Treatment in Air

All of these methods are similar in that the gas at the surface of the substrates is ionized, either with the help of an electric field, or with a chemical reaction. For a differentiation of the different method one has to look at the method of ionization as well as the electron density and the electron temperature generated by the different methods (Figure 1).

Flame Treatment is generated by aiming a combustion flame, typically a propane or butane flame, onto the polymer surface. As can be seen in figure 1 the electron density, and hence the ionization rate, in a flame is at the lower end of plasmas used for surface treatment. The high gas temperature in a flame poses a problem for most polymer surfaces

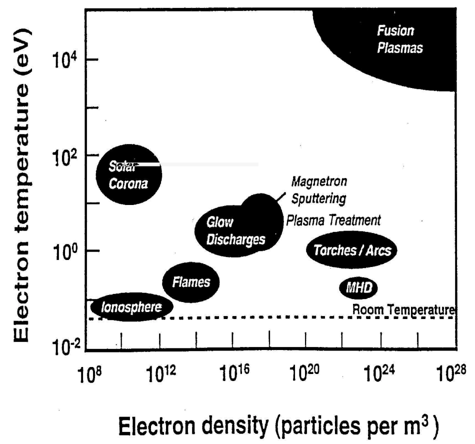

Figure 1: Plasma Classification

In Corona Treatment Systems the ionization is created by applying a high frequency high voltage to an arrangement of two opposing electrodes, of which at least one is insulated with a dielectric. This creates streamer like discharges, which ionize the discharge gap. Corona Treatment is the most widely used treatment for polymer webs in the converting industry. Although the technology has been established throughout, it still bears some major drawbacks: The streamer like discharge is highly non-uniform, and it has been shown, that once a streamer hits the polymer surface, it leaves a local discharge, which in return attracts the next streamer to the exact same spot (4). The result is a localized treatment, the maximum achievable treatment level therefore is an average of the treated areas and untreated areas. A second disadvantage of Corona Treatment is the high voltage required to initiate the discharge. The voltage can be high enough to create a discharge on the backside of fast moving webs, resulting in treatment of the backside as well, an effect not wanted in most cases.

Plasma Treatment in Vacuum: Unlike in Corona Treatment the low pressure levels in vacuum coating chambers allow to generate uniform plasma, usable for highly effective treatment of polymer surfaces. The technology is widely used for web coating application and for the treatment of 3D objects like automotive bumpers. The uniformity of the plasma allows for high treatment levels. Results on such treatments have been reported earlier (7, 8).

Plasma Treatment at Atmospheric Pressure: The high functionality of a uniform plasma discharge in vacuum has driven many efforts to establish a uniform glow discharge at atmospheric pressure, making this technology applicable to processes at atmospheric pressure and hence avoiding expensive vacuum equipment. Efforts have been reported from groups around the world (e.g. 9 and 10). Recently Sigma Technologies International developed a line source, which can produce a stable glow discharge (11).

The differences to a Corona Treatment System are as follows:

- Injection of Plasma Gas directly into the discharge gap. In order to achieve a stable glow discharge free of streamers it is required to use noble gases, whose high metastable phases allow the steady glow discharge. In order to reduce the consumption of these gases to a minimum the gas is injected directly into the discharge gap. Doing it this way also allows to inject other treatment gases, which get highly ionized in the discharge and which allow to address the specific chemistry of the treated polymer.
- Creation of a stable and uniform glow discharge: Unlike Corona, where the discharge occurs in streamers, the APT creates a uniform glow in the discharge gap. This allows for uniform treatment on the polymer surface, thus a higher treatment level of the surface is achievable.
- Lower Voltage: The voltage required to initiate the gas discharge is greatly reduced compared to Corona Treatment Systems. This prevents backside treatment, one of the major drawbacks of Corona.

LONG LASTING TREATMENT ON POLYMER WEBS

- The effect of Atmospheric Plasma Treatment on polymer web surfaces has been investigated with the following materials: Polyethylene (PE), biaxial oriented PolyPropylene (boPP) and Polytretrafluorethylene (PTFE).

Results:

Figure 5 shows the increase in surface energy based on the treatment dosage on PE. The same graph shows the carbon concentration on the surface, with 100% carbon being the level in the untreated sample. It can be seen, that the surface energy drastically increases from about 31 dyne/cm to about 41 dyne/cm at 2 J/cm^2.

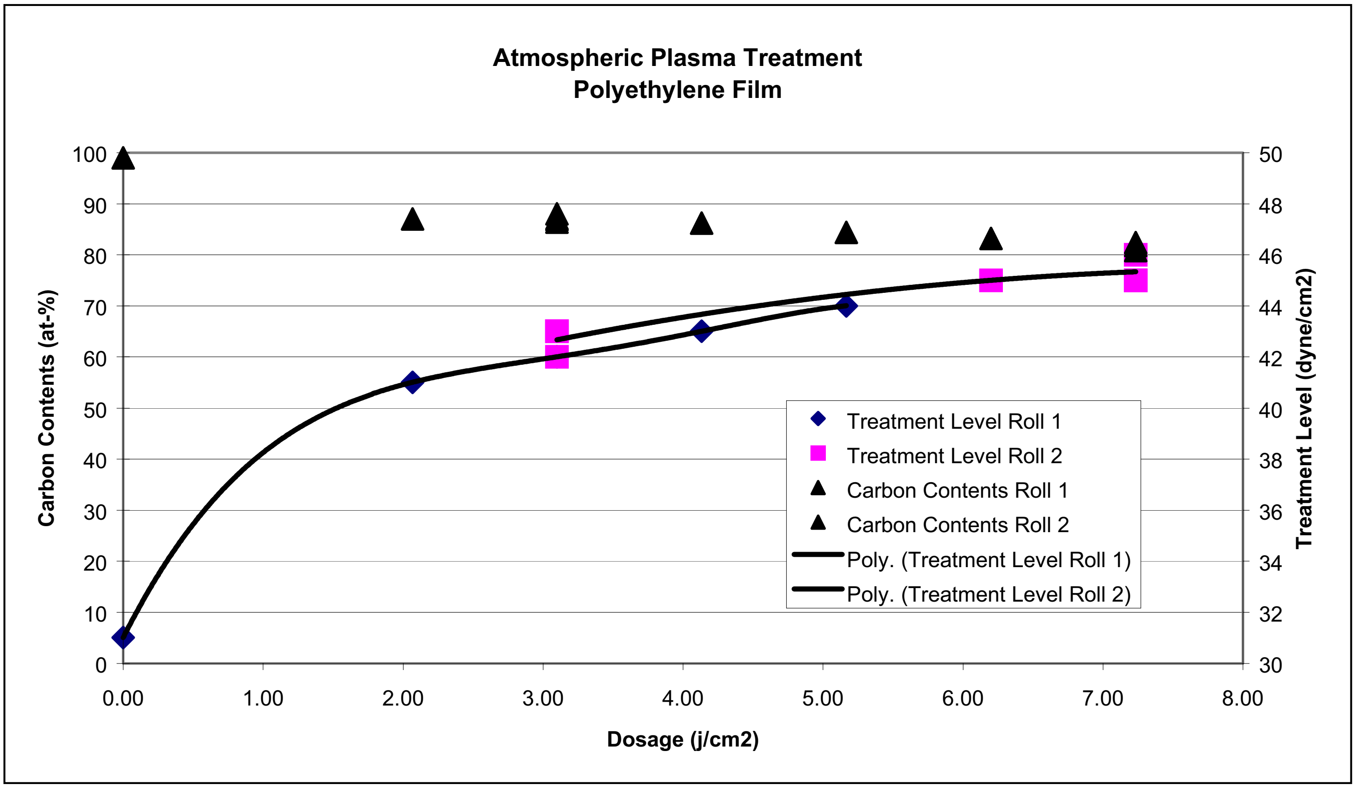

Figure 5: APT Treatment of PE Film

Increasing the dosage leads to a steady increase of surface energy, with a maximum of about 46 dyne/cm at a dosage of 7.5 J/cm^2. At the same time a decrease in the carbon concentration at the surface can be observed, with the missing carbon being replaced with oxygen. The formation of hydroxyl, carbonyl or carboxyl groups are most likely, although have not been confirmed yet.

Looking at the aging effect of the surface treatment (Figure 6) one can see though, that the high treatment level declines over a period of about 500 hours, to settle at a level of about 38 dyne/cm.

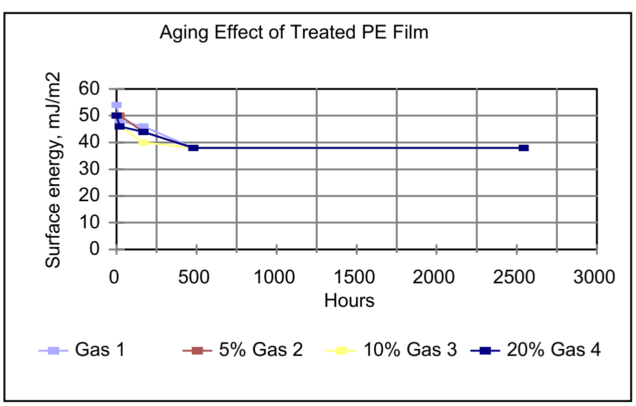

Figure 6: Aging effect of APT Treatment on PE-film

This changes, however, if a mixture gases is used (Figure 7). Not only can a much higher level of surface energy be achieved (60 dyne/cm, but the treatment does not or only slightly decay over a period of 500 hours. This effect can be attributed to a grafting process, meaning that new active chemical groups have been implanted from the acetylene into the surface.

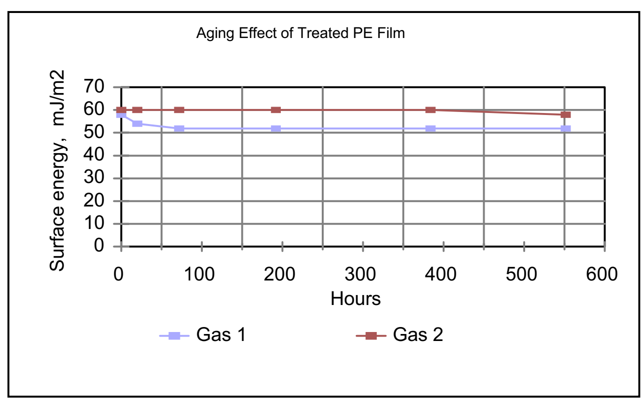

Figure 7: Aging effect of APT Treatment on PE film.

Similar effects can be observed when treating boPP film. Figure 8 shows the increase in surface energy when treating with different dosage levels.

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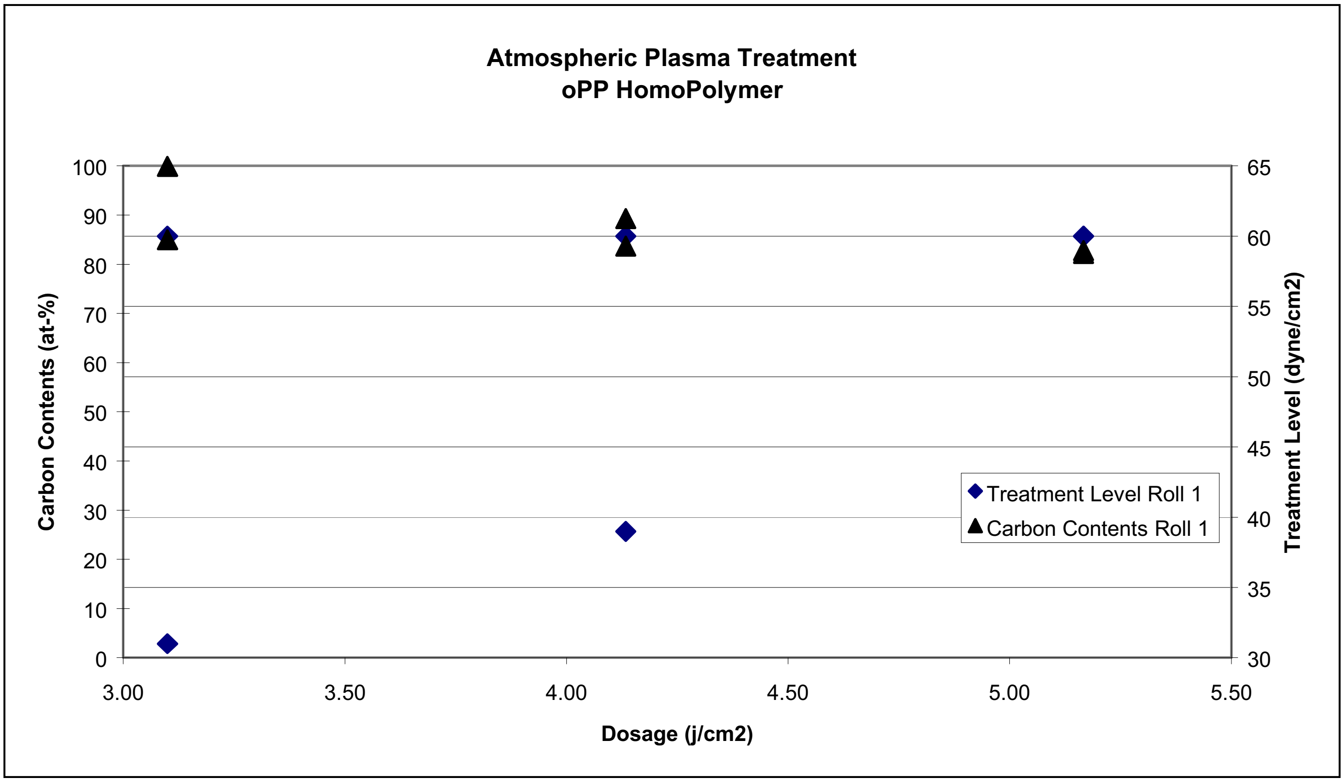

Figure 8: APT Treatment of boPP Film

As can be seen in Figure 8, there are two points with no or only low increase in surface energy. Two different gas flow settings where used during the treatment, with the lower setting basically to low to establish the stable glow discharge. This switches the APT into a standard corona mode, basically exhibiting streamer discharges. After adjusting the gas flow to achieve stable glow discharge a high treatment level (about 60 dyne/cm) could be achieved with the same dosages. Similar to PE a decrease in carbon concentration can be observed with increasing treatment level, again with the difference being replaced by oxygen. The same effects as on PE can be assumed as for the formation of hydroxyl, carbonyl and/or carboxyl groups.

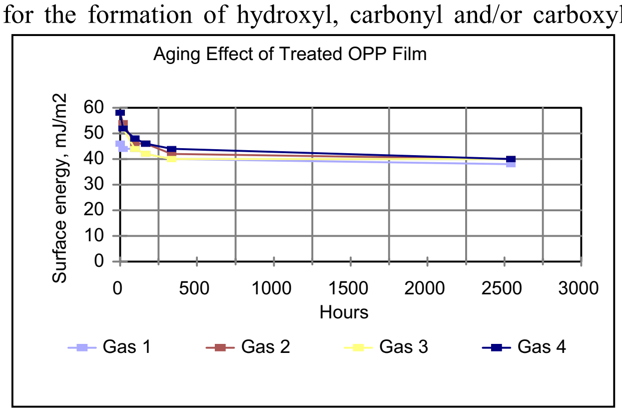

Figure 9: Aging effect of APT Treatment on boPP Film.

As with PE, the treatment achieved with a different gas mixture does not seem to be stable over time (Figure 9). Although the decline is not as rapid as with PE, there still is a steady decline in surface energy until it settles around 40 dyne/cm. Treating the boPP with this mixture again gives results similar to the treatment of PE. In this case however there is no decline observable over a time of 800 hours (Figure 10).

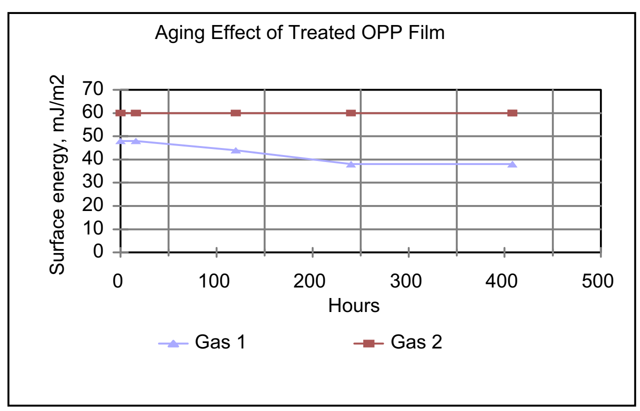

Figure 10: Aging effect of APT Treatment on boPP Film.

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A challenge was the treatment of PTFE. With standard or inert gases a certain increase in surface energy could be achieved, but it only lasted for a few hours, similar to what is known of PTFE treatment with Corona. Treatment of PTFE with other gases however shows very surprising results: Not only is it possible to achieve 60 dyne/cm on the PTFE surface, but the high energy surface is rather stable (Figure 11).

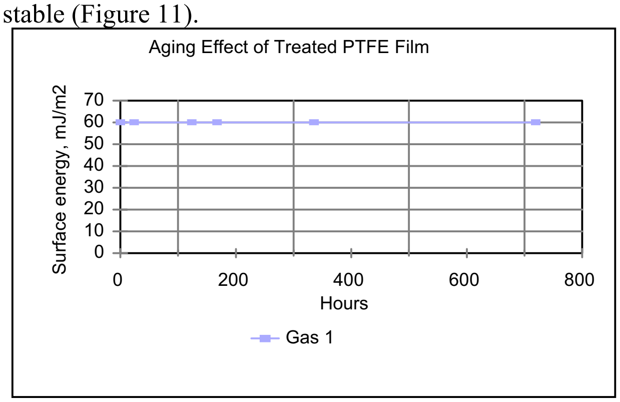

Figure 11: Aging effect of APT Treatment on PTFE film.

CONCLUSIONS

Most polymer surfaces required some sort of activation to allow further processing. I could be shown that with the new Atmospheric Plasma Treatment (APS) high levels of treatment can be achieved. Using specific gas mixtures also allows to create long lasting treatment.

In the future it will be necessary to specify the functionality of the high surface energy levels in terms of printing and adhesion.

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