Increasing the wettability of EVA through a laboratory glow discharge cold plasma reactor treatment

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Abstract

A plasma technique was applied to superficially modify ethylene-vinyl-acetate (EVA) under form of flat sheets, using a laboratory reactor, in order to increase the wettability of the material. The following parameters were varied, in order to assess their influence on wettability: a) exposure time; b) air flow rate; c) voltage.

Among the parameters studied, the most important in determining the wettability was the treatment time. The air flow rate and voltage were far less effective, despite each of these parameters was allowed to vary within a quite large range. The variation in the wettability with exposure time followed a trend well described by a sigmoidal curve: negligible variations in the treated surface were recorded within the first three minutes, whereas the wettability strongly increased afterwards, achieving its maximum value after about five minutes.

Tests were also performed to verify the stability of the treatment after exposure in air at ambient temperature. To this aim, the variation of wettability after the treatment was measured at predefined time intervals. It was found that the effect of plasma exposure is rapidly loosen, with the wettability coming back to the original untreated value within about 15 min. The experimental data showed that the characteristic time of decay depends on both the air flow rate and the voltage used during the plasma treatment. In particular, higher voltages and gas flow rates result in longer decay times. A semi-empirical law, assuming an exponential decay of the wettability with time, was assessed.
Introduction

In recent years, many authors have demonstrated the ability of cold plasma techniques to physically and chemically modify the surface of polymers and inorganic materials. The plasma action on a polymeric surface is very complex in nature, involving the generation of free radicals, molecular interdiffusion, and ablation with increase in microporosity and texture formation. G. Bogoeva-Gaceva [1], I. De Iorio [2], S.L. Perrone [3], B.R.K. Blackman [4], Rongzhi [5], Sung In Moon [6], Wilson Wong [7]. It has been shown that these phenomena increase the surface wettability, resulting in a better adhesion to coatings and adhesives.

The cold plasma method basically consists of a radio-frequency plasma generator, allowing the surface modification through the ionisation of a large gas volume confined in a vacuum chamber together with the material to be treated. Its main drawbacks are high energy dissipation, discontinuity in the process layout, limitations in the material volume to be treated, high cost.

In previous works, a laboratory glow discharge cold plasma reactor, resistively coupled and working under relatively high gas pressure, was demonstrated to result in surface treatment of polymeric and inorganic materials, Tagliaferri [8], de Iorio [2] [10], Leone [9] [11]. Contrary to the usual radio-frequency plasma generators, the ionisation of the gas flow in this appliance is accomplished by means of a low current voltaic arc. The use of this technique offers some advantages, such as localised treatment, low operating and maintenance costs, increased efficiency, possibility of a continuous process.

In this work, the effectiveness of the previous laboratory reactor was verified by using EVA (ethylene-vinyl-acetate) as a material to be treated. EVA was chosen because of the difficulty to bond it by commercially available glues. The wettability, evaluated by measuring the contact angle between the treated surface and H₂O, was assumed as a representative parameter of the surface modification after cold plasma treatment. The effect of the process parameters on the wettability achieved and on its stability after the end of the treatment are presented and discussed.

Features of the cold plasma reactor

The main components of the laboratory glow discharge cold plasma reactor used in the experimental tests are schematically represented in figure 1.

The reactor is essentially made of a sealed chamber, within which two electrodes, 100 mm far and put in a glass chamber for the gas flow and plasma generation, are contained. The gas flow from the plasma chamber (essentially consisting of a tube approximately 8 mm in internal diameter) to the sealed chamber is allowed by a series of small holes, about 1 mm in diameter, put at the top of the process zone and not shown in the figure. The gas flow rate can be changed by suitably setting the working parameters of a vacuum pump; this results in a different degree of vacuum in the sealed chamber, measured by a vacuometer.
Air & et Vacuometer
Sealed chamber

Figure 1: Schematic of plasma reactor.

![Schematic diagram of plasma reactor]

Figure 2: Glow discharge current as a function of gas flow rate, Q, for different supply voltages V (in Volt).

![Graph showing current as function of flow rate and supply voltage]

The electrical circuits are made of a step up transformer, with 1 to 136 ratio, at which secondary the discharge element and a resistance of 1 MΩ are connected. No change in the voltage occurs in the glow during the discharge regime, but a control of the glow discharge current is possible by varying the supply voltage V of the electrical circuit.

In general, the current present in the discharge is a function of both the voltage V and the gas nature and flow rate. However, when air is used, the sensitivity to flow rate Q is negligible (figure 2), especially in the range V = 88 – 176 Volts, which is of interest in the present work. Due to this, where appropriate the current is individuated uniquely by the supply voltage value in the discussion of the experimental results, without specification of the flow rate involved.
Materials and Experimental Procedures

The material used in this work was closed pore ethylene-vinyl-acetate (EVA) under the commercially available form of flat sheets 5 mm in thickness and 200 x 300 mm² in plane dimensions. From the sheets, rectangular specimens having 10 x 50 mm² in plane dimensions were cut, and treated in the home-made, laboratory cold plasma reactor described previously. According to the aims of this work, the parameters varied during the plasma treatment were the supply voltage V (in the range 88 to 176 Volts) at the transformer, the gas flow rate Q (107 to 281 l/min), and the treatment time t (2 to 8 min). In particular, three different flow rates were adopted: 107 l/min, 165 l/min, and 281 l/min, resulting in a vacuum level of 4, 6 and 8 mbar in the reactor sealed chamber, respectively. In all the tests, the gas was technical air. After treatment, the surface wettability was evaluated by measuring the contact angle between the treated surface and a droplet of distilled H₂O by a contact angle analyser, model IMAS CAA3. Preliminary tests showed that the contact angle decreases sensibly with elapsing time after the H₂O droplet is put in contact with the surface under evaluation. Therefore, in all the wettability tests the contact angle measurement was conventionally carried out after a fixed time interval (about 20 s) had elapsed from the droplet placement.

In order to assess the uniformity of the plasma treatment along the length of the process zone, the wettability tests were performed with reference to five predetermined points, labelled by A, B, C, D, E in figure 1, about 10 mm apart one from the other. In particular, the point A was located near the midspan of the process zone.

The aggression of ambient atmosphere may result in modifications in a plasma treated surface, degrading its wetting property. To investigate this topic, wettability tests were also carried out at predetermined intervals of time (referred to as "decay time", tₜ, hereafter) after the plasma treatment. The maximum decay time investigated was tₜ = 15 min. At least six specimens were adopted for each of the experimental conditions previously specified.

Results and discussion

It is well known [12] that the contact angle α is a quantitative parameter correlated with the extent to which a liquid wets a solid. When α is large, the liquid droplet tends to minimise its contact surface with the solid, and the wettability is low. On the contrary, as far as α decreases, the liquid tends to spread over the surface, indicating a good wettability. Increasing the wettability of a solid surface results in better bondability: this explains why the wettability test was adopted in this work to verify the effect of cold plasma treatment on EVA, a material difficult to bond by the commercially available glues. Although a wettability test directly provides the contact angle value, throughout the discussion of the experimental results reference will be made to the quantity
The choice of $\cos \alpha$ is justified by the Young’s equation [12]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \alpha$$  \hspace{1cm} (1)

where $\gamma$ is the surface tension, and the subscripts “s”, “l”, “v” represent the solid, liquid, and vapour, respectively. From equation (1), the actual parameter correlated with the physical phenomenon is $\cos \alpha$.

As stated previously, one of the scopes of the experimental tests was to verify the uniformity of the plasma treatment throughout the process zone. In figure 3, the measured values of $\cos \alpha$ are plotted against the treatment location (figure 1) for the particular condition $V = 176$ Volts, $Q = 281$ l/min, $t = 5'$. For comparison, the wettability of the untreated material (NT) is also shown.

It is seen that all the wettability points concerning a given treatment time are sensibly flat. This indicates that the plasma reactor architecture guarantees a good uniformity in the treatment, which is independent of the location chosen in the process zone. Although not shown here, similar conclusions were drawn from the analysis of the results generated under a variety of process conditions. Therefore, in what follows no distinction will be made between experimental data obtained in correspondence of different locations of the plasma generator.

The points in figure 3 clearly reveal the strong effect that the plasma treatment can have on the wettability of EVA: under appropriate conditions, $\cos \alpha$ dramatically increases compared to the characteristic value of the virgin material. However, in view of an industrial application, the correlation between the operating parameters and the wettability achievable is of concern, affecting not only the bondability of the material, but also the layout and the overall cost of the process.

Figure 4 shows the wettability against treatment time, $t$. Different symbols denote different process conditions, consisting of distinct values of the voltage and air flow rate. Each point is the mean value of six valid experimental tests.

Quite surprisingly, within the ranges of values adopted in this work, both $V$ and $Q$ negligibly affect $\cos \alpha$, despite the large variations in these parameters allowed in the experimental program. On the contrary, the time of exposure to the plasma flow is crucial in determining the surface modification. From the data in Figure 4, the dependence of the wettability on $t$ follows a characteristic trend: only a moderate increase in $\cos \alpha$ is noted within the first three minutes, whereas a steep variation occurs in the interval 3 to 5 min. After that, a complete wettability of the EVA surface is practically achieved.

Of course, the insensitivity of the treatment to $V$ and $Q$ indicates that good results can be obtained in an industrial environment without the use of sophisticated instrumentation for the process control. At the same time, the behaviour observed suggests that cost considerations, rather than technical requirements, should lead to the selection of the actual values of voltage and air flow rate.

Looking at the effect of treatment time, the minimum time required to achieve a complete wettability is conceivable in view of an industrial application.
However, it must be recognised that this critical time hardly complies with a continuous layout, which is one of the potential advantages of the cold plasma compared to the usual plasma technology.

In order to quantitatively express the dependence of wettability on exposure time, a sigmoidal law:

\[
\cos \alpha = \cos \alpha_0 + \left[ \frac{k}{1 + e^{-2(t - \tau)}} \right]
\]  

(2)
was assumed, where \( \cos \alpha_0 \) is the wettability of the untreated material, and \( k, \tau \) two constants to determine experimentally.

The \( \cos \alpha_0 \) value was directly measured, yielding \( \cos \alpha_0 = 0.14 \). The other constants in equation (2) were obtained by the best fit method, using the results in figure 4, giving \( k = 0.82 \) and \( \tau = 3.5 \text{ min} \). The solid line in the figure is the graphical representation of equation (2). The correlation between the theoretical model and the data is reasonable, so that equation (2) can be used to predict the wettability achieved as a function of the treatment time in the case under examination.

An important question, strictly correlated with the possibility to actually apply cold plasma to improve surface wettability of EVA, is whether the variations induced by the treatment are stable with elapsing time after the treatment has been completed. To clarify this topic, some specimens were treated using different \( Q \) and \( V \) values for a treatment time \( t = 5' \), in such a way that the maximum achievable wettability could be reached (figure 4). Then, the samples were exposed to ambient temperature and humidity for predetermined time intervals, after which the wettability was measured anew. Selected results are collected in figures 5a and 5b (referring to two different \( Q \) values), where \( \cos \alpha \) is plotted against the time interval elapsed after the end of the plasma treatment, indicated by the symbol \( t_d \) (decay time). Each curve in the same diagram is characterised by a different \( V \) value. The horizontal lines in the figures represent the wettability of untreated material.

From both the diagrams in figure 5, it is evident that the surface modification induced by the plasma treatment rapidly decays with time. Further, although the increase in \( \cos \alpha \) during treatment is unaffected by the \( Q \) and \( V \) values set (figure 4), the same does not hold for the decay law. The latter is the steeper, the lower are the \( Q \) and \( V \) values adopted during the material treatment. This statement was also confirmed by the experimental results obtained adopting \( Q = 165 \text{ l/min} \), which are not shown here. In particular, it is observed that, when \( Q = 107 \text{ l/h} \) (figure 5b), the effect of plasma is completely loosen within about 15 min.

![Figure 5: Wettability, \( \cos \alpha \), against decay time, \( t_d \), for two different air flow rates, \( Q \): a) \( Q = 281 \text{ l/h} \); b) \( Q = 107 \text{ l/h} \).](image-url)
At this time, the physical reason for the previous behaviour is unknown. However, it is evident that a wettability test immediately after the end of the treatment does not provide an exhaustive information on the variations actually occurring in the surface. As a matter of fact, the effect of V and Q is not revealed by the data in figure 4, whereas it is clearly apparent from figure 5. On the other hand, the rapid decrease in \( \cos \alpha \) suggests that a cold plasma treatment on EVA in an industrial application only makes sense if bonding is carried out within a short time after the exit from the reactor chamber. Alternatively, an effective protection of the surface must be found. To this aim, tests are scheduled presently to verify whether the decay can be avoided by storage under vacuum or protection by plastic films.

To analytically model the decay in wettability with time, the exponential law:

\[
\cos \alpha = k \cdot e^{-\left(t_d - t_0\right)/\tau_d}
\]  

was assumed, where \( k, \ t_0, \ \tau_d \) are constants possibly depending on the process conditions. In particular, \( k \) is the \( \cos \alpha \) value corresponding to \( t_d = t_0 \); the latter parameter physically represents the fact that, as appears clearly from the data in figure 5, the variation in wettability follows a law different from equation (3) in the interval 0 to 2 min, not covered by experimental points because of the minimum time technically required to carry out the first measurement of \( \cos \alpha \). Finally, \( \tau_d \) is a characteristic decay time.

From equation (3), the following relationship is obtained easily:

\[
\log(\cos \alpha) = \log k + \frac{t_0}{\tau_d} - \frac{t_d}{\tau_d}
\]

so that, plotting the data in figure 5 on a log-log scale should result in a straight line having slope \(-1/\tau_d\) and intercept given by the quantity:

\[
a = \log k + \frac{t_0}{\tau_d}
\]

Although not discussed in deep here for lack of space, the analysis of the experimental results through equations (4) and (5) revealed that the constants \( k \) and \( t_0 \) are sensibly independent of the process conditions, yielding \( k = 0.870 \) and \( t_0 = 2.85 \) min in the case examined. The only constant affected by Q and V is the characteristic decay time, which is well described by the relationship:

\[
\frac{1}{\tau_d} = 3^{-6}(Q \cdot V) - 0.182
\]

providing \( \tau_d \) in min when V is given in Volts, Q in l/h.
Conclusions

A cold plasma generator, working in air flow, was used to superficially treat Ethylene-Vinyl-Acetate (EVA) panels, in order to increase their wettability. From the results presented and discussed in this work, the main conclusion are as follows:

- the plasma treatment appears to be able to notably increase the material wettability;
- the wettability achieved is strongly dependent on the treatment time, whereas it is negligibly affected by the voltage and air flow rate, within the ranges of values adopted for the latter parameters in this work;
- the increase in wettability with time can be analytically modelled by a sigmoidal curve;
- if the material is exposed to ambient after plasma treatment, the wettability rapidly decays with time, following an exponential law;
- the characteristic decay time depends on the process parameters, increasing with increasing both the voltage and the gas flow rate.
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References


