

APPLICATION OF ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE PLASMA FOR POLYETHYLENE POWDER MODIFICATION

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Paper refers about a novel plasma reactor exploiting the dielectric barrier discharge (DBD) burning in air at atmospheric pressure by ambient temperature and its usability tests. Test modifications were performed with the high density polyethylene powder Borealis CB 9155-01. Modification effect was evaluated by means of dynamic capillarity rising measurements. Tests proved significant powder capillarity changes. The existence of powder surface changes was also confirmed by ESCA tests. Modification aging effect was remarkably small, hence modification effect is very time stable. In comparison with other in literature described apparatuses used for this purpose the plasma reactor is of a simple construction and needs no vacuum equipment. Its operation costs are low. Described plasma modification method seems to be an appropriate method for plasma modification of polyethylene powder on the industrial scale.
PACS: 52.80. –s

1. INTRODUCTION

Due to its characteristics polyethylene plays important role in industry—it is easy manufacturable and machinable, it is characterized by low wettability, good chemical resistance, high fracture strain and viscosity and it is also physiologically irreproachable. On the other hand polyethylene's nonpolar structure results in its poor paintability, printability and stickiness. To improve these deficiencies, polyethylene has to be treated by various, at present mostly chemical methods, but these are mostly not environmentally friendly and search for alternative methods is urgent.

Polyethylene is produced in form of foils, fibers, films and powder. In the past two decades polyethylene (and other polymers) material surface properties improvement has been extensively studied with methods based on the plasma treatment. Experiments mostly focused on modification of polymer foils, fibres and films, but without distinct success. Research concerned with modification of powders has been less common, probably due to difficult manipulation with the powder during experiments.

For modification of polymer powder surface properties like wettability and adhesion without changing powder bulk properties there have been mostly applied methods employing low temperature ("cold") plasma treatment at low pressures, for citations of the most important reports see Arpagaus et al. [1].

Polymer processing technologies exploiting atmospheric pressure plasma aim at modification of chemical and physical properties of a polymer surface. The change of polymer surface chemical and physical characteristics is provided by functionalization of the polymer. The used gas chemistry depends on the desired surface properties to be imparted, e.g. plasmas containing O₂ increase surface energy by bonding of

O atoms onto the polymer surface, thereby increasing its wettability.

A low-temperature discharge at atmospheric pressure is usually very unstable and it consists of many micro-discharges with a very small radius (each about 0,1 mm). These micro-discharges easily transit to the arc. The easiest way to get a low temperature plasma at atmospheric pressure is DBD. DBD glows between two electrodes separated by a gas gap. At least one of the electrodes is covered by a solid dielectric. When a high voltage is applied to the electrodes, tiny breakdown channels develop in the discharge channel. These micro-discharges are characterized as a weakly ionised plasma. Its energetic electrons provide an effective tool for chemical surface modification. Ultraviolet radiation produced by the DBD at atmospheric pressure is also participant in polyethylene surface properties modification.

The goal of in this paper described experiments was design and investigation of a novel plasma reactor exploiting the DBD burning in air at atmospheric pressure by ambient temperature.

2. EXPERIMENTAL

Atmospheric DBD reactor consisted of the vertically adjustable discharge channel connected with the power supply and control units (Fig. 1). Plasma was generated in the channel confined by two identical rectangular brass electrodes (mutual distance was 11 mm) and two identical glass walls. One of electrodes was covered with a glass plate. There were used two channels with different "active" regions ((9x30) mm cross-section and length 100 mm and 242 mm. During all measurements reactor channel direct axis and reactor base formed an angle 45°. Electrodes were connected to the adjustable high-voltage supply. Plasma reactor was designed as a gravity-fed. For

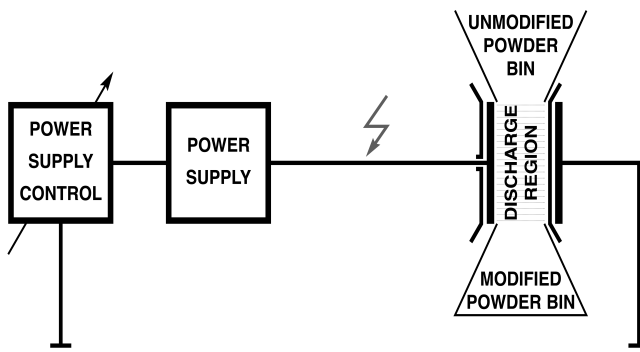


Fig. 1. Schematic view of the experimental apparatus

simulation of larger apparatuses operation, in each experiment the powder batches were repeatedly filled in the discharge channel of the reactor, number of transits through the reactor being one of investigated parameters. Trajectories of powder particles were not straight in the channel and due to very low powder particle mass and forces acting in the channel most powder particles moved downward to its bottom on randomly “stirring like” trajectories.

The precise measurement of the particle modification time was hardly practicable, nevertheless the modification time corresponding to one transit through the reactor could be estimated not longer than 1 s.

Modification in atmospheric dielectric barrier discharge was performed in stationary air under atmospheric pressure (743...754) torr, room temperature (20...23) °C and humidity 35-57%.

For tests the high density polyethylene powder Borealis CB 9155-01 was used.

The wettability of this powder was determined with a tensiometer from dynamic capillarity rising measurements according to the Washburn method [2]. Examined powder had been soaked up with the test liquid (benzyl alcohol) while simultaneously the suction velocity was determined and used for capillarity values calculation.

For all measurements the Fraunhofer Institute measuring unit HBM MVD 2555 was used.

Modification effectivity presented by capillarity increase (100% corresponds to the capillarity of unmodified powder) is shown in Fig. 2. All tests except 050202 were performed in the longer reactor channel.

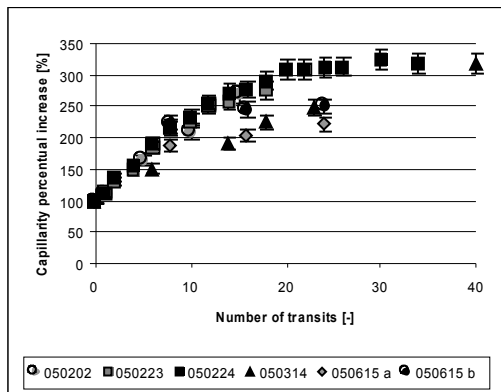


Fig. 2. Dependence of the modification effectivity on number of transits through the reactor channel (for both types regardless the difference of their lengths)

Modification in both types of channels (Fig. 2) shows similar capillarity percentual increase, i.e. modification effectivity. In case of small number of passages (up to fifteen) the modification effectivity seemed to be similar for both of channels, despite of difference of their lengths. Test proved existence of some “saturation” limit, behind it no other capillarity increase was observed. Definition of capillarity “saturation” limit position might be connected with the composition of the air in the plasma reactor channel, and also the method used for powder batch manipulation.

Important aspect for practical application of plasma-modified powder is the modification effect time-stability. Powder wettability changes induced by modification were tested almost during one year after the modification date. The plot of aging expressed by powder capillarity–time relation for samples of various powder batches with maximum number of transits is shown in Fig. 3. Modification effect reduction was very small, most changes seemed to occur in the first 100 days after the modification date. In later dates after modification modified powder wettability values remained stable. Such a long time stability (20% drop after more than one year) of the modification effect was probably up to now not referred in connection to any other way of the high density polyethylene powder plasma modification and is remarkable. Our initial capillarity drop seemed to be smaller than results described in [1], reporting about modification of a similar type of polyethylene powder, but in a plasma downer reactor and about aging test during only 40 days after modification.

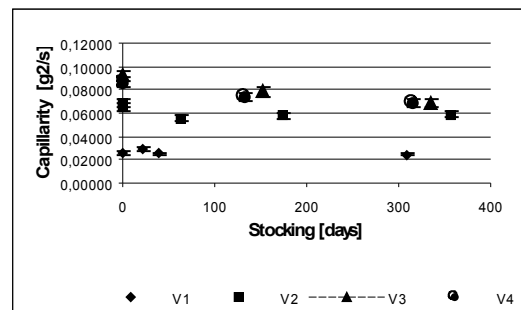


Fig. 3. Modified powder capillarity changes during stocking

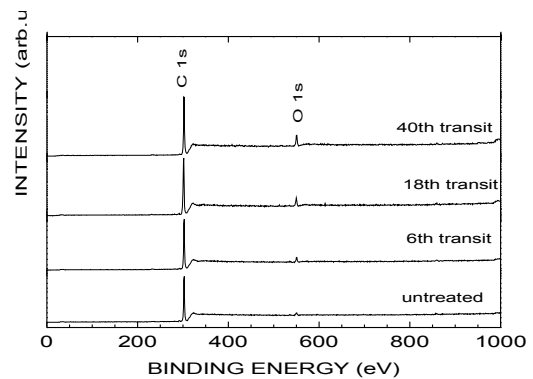


Fig. 4. ESCA results of the air plasma treated Borealis CB 9155 powder in the DBD plasma reactor (samples 050314)

After plasma treatment polyethylene powder chemical state and changes of its surface characteristics were also tested by the ESCA spectral analysis method. Existence of single intense carbon C-1s Peak, characteristic for basic untreated polymer, was distinct in this scan of unmodified powder (see Fig. 4).

Existence of oxygen on the powder surface, that appeared after plasma treatment is considered as one of proofs of the powder surface modification efficiency. In the modified powder ESCA scan there was evidently present the oxygen O-1s peak (Fig. 4); its maximum grew in dependence on the number of transits through the discharge channel.

Existence of new functional groups created by plasma incidence at the modified powder surface was confirmed not only by ESCA results but also by additional calculations of chemical states representation and electron bond energies.

CONCLUSIONS

Paper refers about a novel plasma reactor exploiting the dielectric barrier discharge (DBD) burning in air at atmospheric pressure by ambient temperature and its usability tests. Test modifications were performed with the high density polyethylene powder Borealis CB 9155-01. Modification effect was evaluated by means of dynamic capillarity rising measurements. Tests proved significant powder capillarity changes. The existence of powder surface changes was also confirmed by ESCA

tests. Modification aging effect was remarkably small, hence modification effect is very time stable. In comparison with other in literature described apparatuses used for this purpose the plasma reactor is of a simple construction and needs no vacuum equipment. Its operation costs are low. Described plasma modification method seems to be an appropriate method for plasma modification of polyethylene powder on the industrial scale.

ACKNOWLEDGEMENT

This project was supported by projects of the MSM 1M0577

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ПРИМЕНЕНИЕ ПЛАЗМЫ ДИЭЛЕКТРИЧЕСКОГО БАРЬЕРНОГО РАЗРЯДА ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ ДЛЯ МОДИФИКАЦИИ ПОЛИЭТИЛЕНОВОГО ПОРОШКА

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Описан новый плазменный реактор, в котором используется диэлектрический барьерный разряд в воздухе комнатной температуры при атмосферном давлении, и результаты его испытаний. Проверка эффективности реактора была проведена с полиэтиленовым порошком большой плотности типа Borealis CB 9155-01. Эффект модификации оценивался с помощью измерений динамики роста капиллярности. Испытания показали значительные изменения капиллярности порошка. Наличие изменений поверхности порошка было подтверждено данными измерений с помощью метода ESCA. Влияние на скорость старения оказалось необыкновенно слабым, т.е., эффект модификации является стабильным во времени. По сравнению с используемыми для этой цели устройствами, описанными в литературе, предлагаемый плазменный реактор имеет простую конструкцию и не нуждается в вакуумном оборудовании. У него – низкие эксплуатационные расходы. Описанный метод плазменной модификации представляется подходящим для использования плазменной модификации полиэтиленового порошка в промышленных масштабах.

ЗАСТОСУВАННЯ ПЛАЗМИ ДІЕЛЕКТРИЧНОГО БАР'ЄРНОГО РОЗРЯДУ ПРИ АТМОСФЕРНОМУ ТИСКУ ДЛЯ МОДИФІКАЦІЇ ПОЛІЕТИЛЕНОВОГО ПОРОШКУ

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Описано новый плазменный реактор, у якому використовується діелектричний бар'єрний розряд у повітрі кімнатної температури при атмосферному тиску, і результати його іспитів. Перевірка ефективності реактора була проведена з поліетиленовим порошком великої щільності типу Borealis CB 9155-01. Ефект модифікації оцінювався за допомогою вимірів динаміки росту капілярності. Іспити показали значні зміни капілярності порошку. Наявність змін поверхні порошку було підтверджено даними вимірів за допомогою методу ESCA. Вплив на швидкість старіння виявився незвичайно слабким, тобто, ефект модифікації є стабільним у часі. У порівнянні з використовуваними для цієї мети пристроями, описаними в літературі, пропонується плазмовий реактор має просту конструкцію і не має потреби у вакуумному устаткуванні. У нього – низькі експлуатаційні витрати. Описаний метод плазмової модифікації представляється підходящим для використання плазмової модифікації поліетиленового порошку в промислових масштабах.