POLYMER POWDER ADHESION TO METALLIC SURFACE IMPROVEMENT WITH PLASMA

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Useful method for corrosion prevention is coating of a base material with a suitable substance. It performs a barrier between the base material and its environment. Great attractions in this field have found polymers, among them polyethylenes (PE). Due to the low adhesion grade of unmodified polymer powder or granules the application of any modification process increasing the adhesion grade is crucial. At present there is no universal approach to polymer adhesion improvement and there have been employed various quite different techniques. Our research employed the PE adhesion improvement by plasma modification. There were used two plasma reactors – the microwave low pressure reactor and the atmospheric reactor employing dielectric barrier discharge (DBD). The adhesion of the powder was determined by measurement of strength force demanded for displacement of the PE-metal joint.

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1. INTRODUCTION

Effective method for corrosion prevention is the coating of a base material with a suitable substance that extends the base material persistence against corrosion for a much longer time period than in case without protection. Coating shelters base material by performing a barrier between it and its environment. To provide adequate corrosion protection, the coating should be uniform, well adhered, pore free and self-healing for applications where physical damage to the coating might occur.

In spite of some improper characteristics (in particular a very low surface energy and poor surface adhesion quality) polymers, have found attractions in this field, especially due to their excellent corrosion resistance, competitive cost, low weight, easiness of installation, and higher specific strength than many other materials [1]. Technology of the protective layer deposition incorporates also smelting of the polymer on the substrate. Polymer is mostly delivered in form of powder or granules. For technical requirements adhesion grade can be expressed e.g. by force needed for detachment of joint of two materials.

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Our research focused on the polyethylene (PE) adhesion improvement by plasma modification. There were used two plasma reactors – a microwave low pressure one and an atmospheric reactor employing the dielectric barrier discharge (DBD). For evaluation of PE adhesion to a metallic surface we used a method based on a test method described in [2].

2. EXPERIMENTAL

2.1. MW DOWNSTREAM SYSTEM [3]

Principle of the downstream system was as follows: plasma was generated upside the reactor, below was placed powder under modification. This arrangement prevented temperature-sensitive treated powder from significant overheating. Treated PE powder batch was inserted into the plasma containing radicals stream. To prevent or reduce the recombination of particles of radicals during their movement to the powder batch location, discharge parameters had to be carefully adjusted.

Used set-up consisted of vacuum process chamber made from stainless steel cylinder. Inside the reactor a stainless-steel blender with a horizontal propeller stirrer was placed. The stirrer axis was brought out from the reactor through a vacuum trough-out placed at the reactor bottom. A sealing lip prevented penetration of the powder into the bearing. An electrical engine placed outside the reactor drove the propeller via a vacuum throughout and a vertical movable shaft. This construction enabled distance variation between the blender and the plasma source. Electronic system set the stirrer's speed. In most experiments approx. one revolution per second was used.
2.2. ATMOSPHERIC DBD PLASMA REACTOR [4]

Atmospheric DBD reactor consisted of vertically adjustable discharge channel connected with power supply and control units (Fig. 2). Plasma was generated in cuboidal discharge channel confined by two identical large rectangular brass electrodes (interelectrode distance was 11 mm) and two identical glass walls. One of the electrodes was covered with a glass plate 2 mm thick. The channel dimensions were (9x32x242) mm.

PE powder particles moved along reactor vertical axis, particle trajectory in this direction was at least 242 mm. Plasma reactor channel position was adjustable round its vertical axis. For powder modification time prolongation during a single transit through the reactor, channel vertical axis and the reactor bottom formed an angle 45° during all measurements.

Plasma reactor was designed as gravity-fed, i.e. due to the gravity force continuous stream of powder particles passed through the reactor channel from a hopper at the top of the channel to a collecting bin at its bottom. For simulation of larger apparatuses operation (i.e. with longer “active zone” resulting in lengthier modification time during one transit), every powder batch was repeatedly thrown through the discharge channel of the plasma reactor; number of transits through the plasma reactor was one of the investigated parameters. Precise measurement of the particle transition time through the reactor, i.e. modification time, was hardly executable because of indirect powder grain trajectories through the discharge channel; nevertheless the modification time corresponding to one transit through the reactor could be estimated as less than 1 s. Thus the total modification time can be estimated by product of the modification time corresponding to one transit and number of transits through the reactor.

2.3. TESTS

The series modification tests were carried out. The PE powder Borealis CB 9155 used as the test medium was characterized with particle average diameter 250 μm, powder density 924 kgm⁻³ and the mass specific surface area of 0.033 m²g⁻¹.

All experiments in MW reactor were performed in stationary air under pressure 100 Pa and room temperature (20–23)°C. Treatment time was (60–600) s. Modification in atmospheric DBD was performed in stationary air under atmospheric pressure (743 – 754) Torr, room temperature (18 – 25) °C, and humidity 35-57%. Modification tests were performed with discharge power of about 150 mW [at (21.0±0.5) kV, 50Hz]. Powder mass flow through the reactor could be estimated as 0.07 kgs⁻¹. Powder used for aging tests was stocked in darkness at room temperature (20 – 23) °C, relative humidity (30 – 40)% in air, but not in the laboratory atmosphere, in closed PE bags.

The adhesion of the powder was determined by measurement of strength force demanded for displacement of the PE-metal joint. Tests were performed in our facility inspired by [2]. There were used polished stainless steel substrates. Specimens were created by smelting powder on the substrate. Force necessary for the separation of the polyethylene from the substrate was measured by a shredder. For comparison the adhesion between the stainless steel and special PE copolymers were determined, too.

3. RESULTS

Adhesion values of different polymers deposited on the polished stainless steel substrates are shown in Fig. 3.

Maximum reached tensile strength value of the unmodified powder was about 2MPa. Values obtained for modified Borealis PE powder varied mostly between (6–7) MPa. For comparison the adhesion strength of commercially produced PE-copolymers fabricated for metal coatings:

a) Flamulit F-HTC 214 (produced by DuPont) and designed for corrosion protection of metal substrate, 
b) Microthene RL MR SP010, (produced by Equistar Chemicals LP) for interlayer deposition by PE coatings were analysed, too. (These PE-copolymers were probably chemically modified.)

The adhesion grade of the plasma-modified conventional polymer was higher than that reached for Flamulit. Our modified Borealis adhesion values were lower than that of Microthene, but we have to keep in mind that Microthene polymer had been specially designed for adhesion layers to steel substrates. Very important aspect for practical application of plasma-modified powder is the modification effect time-stability (aging), tested by powder wettability measurements [3,4].
Fig. 4. Modified powder capillarity stability during stocking. (i.e. aging)

Powder wettability changes induced by modification were tested almost during 800 days after the modification date. The plot of aging expressed by powder capillarity stability of various powder batch samples is shown in Fig. 4 (100% corresponds to the day of modification). Modification effect reduction was very small, most changes seemed to occur in the first 100 days after the modification date. In this period capillarity values of individual samples had dropped modestly and then remained stable, maximum drop after more than 700 days after the modification date was about 20% [3,4].

Modified powder characteristics stability is remarkable and promising for prospective exploitation. Described long time stability (20% drop after more than two years) of the modification effect was probably up to now not referred in connection to any other way of the polyethylene powder plasma modification.

4. SUMMARY

The results of research employing plasma interaction with surface of the PE powder Borealis and its effect on PE powder adhesion to the metallic surface are presented.

For PE powder plasma treatment there were used two plasma reactors. The first one, constructed in the downstream configuration exploited microwave low-pressure plasma and in the second reactor burnt atmospheric dielectric barrier discharge in air at room temperature.

Plasma modification increased polymer powder adhesion to the metallic surface. Adhesion grade of plasma modified powder samples compared with that of routinely chemically treated polymer powders used on industrial scale showed that adhesion of plasma treated samples was almost approaching that of chemically treated ones.

Aging effect during more than 700 days is remarkably small, i.e. modification effect is very time stable.

Described methods might be appropriate for plasma modification of PE powder on industrial scale.

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REFERENCES


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