High-Density Polyethylene Coating on Carbon Steel by an Electrostatic Powder Spray System

MOHAMMAD ALI GOLOZAR,[1] ROUHALLAH BAGHERI[2]

[1]Department of Materials Engineering, Isfahan University of Technology, 84154 Isfahan, Iran

[2]Department of Chemical Engineering, Isfahan University of Technology, 84154 Isfahan, Iran

ABSTRACT: Plain carbon steel specimens were surface-treated mechanically and then chemically before applying high-density polyethylene (HDPE) coating. Pretreated specimens were coated with HDPE powder, both with and without a heat stabilizer (Irganox 1010), using a spray electrostatic technique. Effects of various variables, such as surface roughness, prephosphating treatment, addition of stabilizer, and the role of curing time and temperature were investigated. Mechanical and immersion tests were conducted to measure adhesion, ductility, and corrosion resistance of the coated specimens. Scanning electron microscopy and infrared spectroscopy were used to study the microstructure of produced coating and its interface with the substrate, as well as the possible chemical changes that occurred. The results obtained revealed that, pure HDPE can be coated on plain carbon steel with a good performance. It was further observed that an addition of 0.5 wt % of heat stabilizer to HDPE powder increases the performance of produced coating significantly. This was evidenced by the measurements of adhesion, ductility, and corrosion resistance in sulfuric acid, sodium hydroxide, ferric chloride, water, and salt spray, as well as scanning electron microscopic examinations and infrared spectra. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2507–2513, 1998

Key words: high-density polyethylene; coating; spray electrostatic; carbon steel; adhesion ductility; corrosion resistance

INTRODUCTION

Using polymeric coatings is one of the important and effective ways to prevent corrosion of various metallic materials, including plain carbon steel.[1] To obtain strong adhesion between the polymer and substrate, spreading the polymer melt over the pretreated metallic surface is essential. It has been shown that a zero contact angle is required for a very good spreading of the liquid on the solid.[2] Thermodynamic characterization of the solid surface by contact angle measurements provides their surface energy [i.e., dispersive and nondispersive (including Debye, Keeson, and acid–base interaction) compounds of this energy].[3] Recent work considers that only London dispersion and hydrogen bond forces are significant in adhesion between adjacent phases.[4] Surface energies and hence the extent of contact between substrate and polymer coatings are a function of the chemical nature of the polymer and metal surface characteristics. The relationship between surface energies and wetting equilibria have been studied by many authors.[2,5–7] Also, a good relationship between bond strength and the polymer's surface energy has been found.[8]

The high-energy solid surfaces (i.e., metals and oxides, 500 mJ m^{-2}) would be readily wetted by polymer coatings. With value of surface energies typically less than about 50 mJ m^{-2} (23.5 mJ m^{-2} for polyethylene) giving a high degree of intimate interfacial contacts. However, several factors may affect the bonding operation, depending on the exact circumstances. These factors may all give rise to a weak boundary layer on the surface of the metals and thus prevent the attainment of a good adhesion.[9] Therefore, before applying the polymer on the surface of the metal, a surface pretreatment of the substrate is vital. The objectives of this treatment are: (1) elimination of impurities and weak boundary layers and (2) modification of the chemical composition and surface morphology.

It has been shown[10] that, as a result of these operations, the substrate surface energy is generally increased. In this respect, surface roughness as well as surface topography are reported to be very important.[5,10]

It is well known that a high initial adhesion strength is not the only important property of metal–polymer bonds. Of even more importance is durability, especially if the compound is to be exposed to corrosive and/or humid environments. In this respect, the corrosion rate of coated metallic substrate is influenced by many factors. These factors can be grouped as (1) environmental parameters, (2) coating nature, and (3) metal/coating interfacial conditions. Regarding the environment, parameters such as processing variables (stresses, time, and temperature), humidity, and the presence of attacking ions in the vicinity of a coated substrate is described.

Referring to the nature of the polymer coatings, various factors such as chemical composition, molecular characteristics, size distribution of powders in powder coatings, ductility, and permeability are outlined.

Regarding interfacial conditions, maintenance of coating, adhesion, and/or bond strength—especially in the presence of water and various aqueous electrolytes—are generally recognized as prime importance and as prerequisites for maintenance of corrosion protection.[9] The quality of polymer coatings, as well as its bond strength, is a function of variables such as method of applying, time and temperature of curing, surface preparation, additives, and primers.

Rheological properties of polymer melt also have an effect on wetting, film formation, and adhesion on the substrate.[11] The flow of high-density polyethylene (HDPE) melt (pseudoplastic) is characterized by the viscosity, which depends on a number of intrinsic properties of the polymer. It also depends on temperature, decreasing rapidly as the temperature increases.[12] Thus, the higher temperature leads to an easier flow of the polymer melt on the surface. It is the aim of this article to investigate the quality of HDPE coating produced by spray electrostatic techniques. The ability of this coating to prevent corrosion of plain carbon steel in various conditions is also studied.

EXPERIMENTAL

Materials

Substrates and plain carbon steel (st37) were supplied by Isfahan Steel Plant (Isfahan, Iran). Coating material and commercial HDPE (HD6070) containing no additives was supplied by the Iranian Petrochemical Complex Ltd. The tetranuclear phenolic antioxidant, heat stabilizer, under the commercial name of Irganox 1010, was obtained from Ciba Geigy Ltd. (Basel, Switzerland). Zinc phosphate solution, sulfuric acid, ferric chloride, and sodium hydroxide solution were purchased from Merk Chemical Company (Darmstadt, Germany).

Procedure

Flat specimens, 20 × 100 mm dimensions, were prepared from plain low carbon steel sheet, having 2.5 mm thickness. To remove all surface oxides, debris, and greases, primary mechanical and chemical surface cleanings were performed. Regarding the adhesion and bond strength of polymers on metals, surface cleanness is believed to be of great importance. To obtain various surface roughnesses, specimens were subjected to shot pinning (in a shot blast machine), as well as polishing on 100 and 1200 grit size sand papers (using a manual polishing equipment). Surface roughnesses were then measured using a roughness testing machine (Surtonic-3, Denmark). Specimens were then grouped according to the obtained surface roughness results.

After mechanical roughening, the following surface chemical cleaning was performed: (1) immersing in 50°C degreasing alkaline solution for 5 min; (2) washing in distilled water; (3) immersing in 5 vol % of sulfuric acid solution, at 40°C for 1

min; and (4) washing in plenty of distilled water and then dried, using hot air.

Apart from mechanical roughening and chemical cleaning, a number of specimens were subjected to zinc phosphating treatment. For this purpose, specimens were immersed in 60°C zinc phosphate solution for 5 min, washed in distilled water, and finally dried using warm air.

To eliminate the harmful effect of any residual moisture, all specimens were heated at 100°C for 20 min before coating treatment.

Electrostatic powder spray system was used to apply coatings. During the operation, polymer powder was supplied to the spray gun from a feeder unit, where the powder was stored for use. The spray gun directed the powder toward the part to be sprayed in the form of a diffused cloud. Propelling force is provided both by air used to transport the powder from the feeder unit to the spray gun, and by the electrostatic charge imparted to the powder at the gun. Electrostatic voltage was supplied to the spray gun by means of a source designed to transmit high-voltage, low-amperage electrical power to an electrode(s) attached to the spray gun. The diffused, electrostatically charged powder cloud near the grounded part created an electrical field of attraction, thus drawing the powder particles to the part and creating a layer of powder on the part. Powders consisted of pure HDPE and the mixture of HDPE with 0.5 wt % of a heat stabilizer (Irganox 1010). All coated specimens were then subjected to primary curing in air at 60°C for 15 min and secondary curing in the absence of oxygen at 220°C (for pure HDPE) and 230°C (for the mixture of HDPE and stabilizer) for 45 min. The previously described time and temperature of curing were obtained by performing a number of experiments using a wide range of time and temperature. The thicknesses of the coatings were then measured and found to be within the range of $350-400 \mu m$.

Adhesion of coatings on substrates and their ductility was measured using a standard reciprocal scratch test (ASTM D2197) and a standard bending test (ASTM D486), respectively. In the former case, the load needed for coating/substrate separation was measured. Conversely, in the latter case, using a 6–50 mm U-shaped punch, ductility of coating (E) was calculated from equation $E = 100T/(D + T)$. In this equation, T is the sum of coating and substrate thickness, and D is diameter of the used punch. This calculation is based on the smallest punch diameter for which coating cracks.

The resistance of coating against various environments, as well as the corrosion behavior of steel substrates, were assessed by performing: (1) salt spray test (ASTM D117); (2) water immersion test (ASTM D870); and (3) immersion tests in various alkaline and acid solutions, such as 20 vol % sulfuric acid, 32 vol % sodium hydroxide, and 50 vol % ferric chloride solutions.

Scanning electron microscopy (SEM; Phillips Company, model XL30), was used to study the quality of produced coatings, as well as the substrate/coating interfacial nature. In addition, infrared spectroscopy (Shimadzu model 435) was used to investigate whether or not chemical changes occurred after curing, as well as during environmental corrosion tests.

RESULTS AND DISCUSSION

Visual and SEM observations, as well as adhesion and ductility test results, showed that quality and performance of HDPE coatings are highly dependent on curing time and temperature. This is accordance with the results published previously.[13,14] Curing at low temperatures (e.g., < 180°C) needs very prolonged time for good quality coating to be formed. In this respect, at a curing temperature lower than 130°C, no acceptable adhesion was obtained, even for a very long curing time. Conversely, at a high curing temperature (e.g., > 250°C), intensive degradation, blistering, and surface waving of unstable coating were observed. Previously described results were observed on specimens subjected to a 60-min coating period. Regarding the observations and results obtained from experiments performed on coatings cured at various temperatures within the range of 130–250°C, a secondary curing temperature of 220°C was selected for pure HDPE coating, and 230°C was selected for the mixture of HDPE with the heat stabilizer to investigate the effect of curing time.

Results obtained from ductility and adhesion measurement tests performed on coatings cured at 230°C, for various periods of time, are shown in Figures 1 and 2, respectively. As observed, up to 45 min curing time for both ductility and adhesion increased rapidly. Conversely, for a curing time > 45 min, ductility decreases (Fig. 1) while adhesion remains almost constant (Fig. 2).

SEM observations revealed that, at a curing temperature of 220°C, the appearance and quality of pure HPDE coatings also depend on the

Figure 1 Effect of curing time on ductility of HDPE coating containing stabilizer produced on plain carbon steel; curing temperature: 230°C.

curing time. For a low curing time, such as 30 min, unmelted crystallites within the coating were clearly observed. Due to this occurrence, a high porous coating was produced. An example of this type of defect is shown in the SEM micrograph of Figure 3. It is worth mentioning that the density of porosity increased as time and/or temperature of curing decreased. In the case of pure HDPE, increasing the secondary curing time and temperature up to 45 min and 220°C, respectively, decreased the density and/or size of porosities and finally eliminated them. Similar results observed regarding the effect of secondary curing time and temperature on the appearance and nature of HDPE coatings have a 0.5 wt % heat

Figure 3 SEM micrograph showing unmelted HDPE crystallites on the surface of a pure coating; secondary curing time and temperature: 30 min and 220°C, respectively.

stabilizer. An example of a porosity-free good quality coating is shown in the SEM micrograph of Figure 4. Substrate/coating interfaces were also studied using SEM. Results obtained showed that the quality of interfaces was highly dependent on curing time and temperature. An example of a good substrate/coating interface (obtained at a curing time and temperature of 45 min and 220°C) is shown in the SEM micrograph of Figure 5.

Figures 6 and 7 show the effect of surface roughness, zinc phosphate prelayer, and heat stabilizer on the adhesion and ductility of HDPE

Figure 2 Effect of curing time on adhesion of HDPE coating with stabilizer produced on plain carbon steel; curing temperature: 230°C.

Figure 4 SEM micrograph showing a pure HDPE coating without porosity; secondary curing time and temperature: 45 min and 220°C, respectively.

Figure 5 SEM micrograph showing a good quality substrate/coating interface, pure HDPE coating; secondary curing time and temperature: 45 min and 220°C, respectively.

Figure 7 Effect of surface roughness, zinc phosphate prelayer, and heat stabilizer on ductility of HDPE coating on plain carbon steel; secondary curing temperature: 230°C.

coating, respectively. From the results obtained, it is clear that adhesion and ductility of coating are functions of surface roughness. In addition, it is observed that the maximum adhesion and ductility are usually obtained within a range of surface roughness, corresponding to mechanical polishing on 1200 grit size sandpaper, with a mean roughness of 1 μm. Compared with this value, decreasing or increasing the surface roughness would decrease both ductility and adhesion. This effect can be argued regarding the extent of surface wetting action, which is a function of surface-

Figure 6 Effect of surface roughness, zinc phosphate prelayer, and heat stabilizer on adhesion of HDPE coating on plain carbon steel; secondary curing temperature: 230°C.

free energy.[9] It is believed that, below the mean surface roughness of 1 μm, the increase in surface roughness (from 0.4 to 1 μm) would increase the surface-free energy and thus the surface-wetting action. Therefore, the adhesion and ductility would increase.[5,10] Conversely, beyond the mean surface roughness of 1 μm, the increase in surface roughness would decrease the surface-free energy and thus the surface-wetting action. Therefore, adhesion and ductility would decrease.[2,5,7] Thus, it is believed that the topographic nature of the roughened surface can have a determined effect on the adhesion and ductility of coating.[9] Although there are many studies in the literature that report lower adhesion to rough surfaces, there are well-established examples in various types of systems of the opposite effect.[5]

Figures 6 and 7 also show that a pre-zinc phosphating treatment increases the adhesion and ductility of coating to a certain degree. It is believed that the role of the phosphate prelayer is mainly to increase the roughness of specimen surface rather than playing as a binder between HDPE and the substrate.[15] Therefore, it increases the surface-free energy of the substrate. In addition, phosphating would prevent the cleaned substrate surfaces from contamination and thus increase adhesion of the coating onto the surface.

During the curing stage at 220°C for 45 min, the polymer melt viscosity is low enough to provide good contact between macromolecules and the substrate.[5] To achieve a close intimate con-

Figure 8 Weight loss results in ferric chloride solution.

tact with the metal surface, the polymer melt should flow easily, so that it spreads rapidly and wets the surface. It is believed that wetting and molecular diffusion are kinetic means. However, the mechanism of adhesion on the surface is thermodynamic adsorption.[10]

It has been shown that, when hot melted polymer is applied to a solid surface such as metal substrate, the quality of adhesion is usually dependent on conditions that enable the polymer to oxidize.[16,17] The results presented in Figures 6 and 7 reveal that pure HDPE-coated specimens show good adhesion and ductility. This is believed to be due to the physical adsorption between polar groups formed during thermal oxidation of polyethylene (i.e., —C=O) and the substrate. It was also observed that (Figs. 6 and 7) an addition of 0.5 wt % of Irganox 1010 to HDPE powder increases adhesion and ductility of coating substantially. This could be due to the physical bond formation between the substrate surface and the hydroxyl groups of the stabilizer, as well as the polar groups of thermal-dissociated stabilizer.[18] Another reason for the beneficial effect of stabilizer on the improvement of ductility and adhesion could be due to the higher molecular weight of HDPE coating containing stabilizer. This stems from the thermal oxidation prevention of polymer and subsequent halting its chain scission.[12,19] This fact is evidenced from infrared spectra that clearly show no carbonyl formation (at 1720 cm^{-1}) during the two stages of curing.

Results obtained from immersion tests in chemical corrosive solutions revealed a good corrosion resistance behavior of all coated samples.

However, specimens coated with HDPE containing 0.5 wt % heat stabilizer showed a much better corrosion resistance. The coated specimens immersed in 42°C sulfuric acid solution for 61 days were inspected daily and found that, in the case of defect-free coatings (examined by SEM), the polymer can protect the substrate from corrosion perfectly. Results obtained from weight loss measurements, as well as visual and SEM inspections, showed neither corrosion of substrates nor separation, cracking, or blistering of coatings after 61 days exposure time. Infrared spectra of these samples indicate that no structural changes occur during corrosion tests.

Regarding the 32 vol % sodium hydroxide solution, after 64 days exposure, no effect of coating deterioration was observed at all. This was true for HDPE coatings with and without stabilizer.

Results obtained from weight loss measurements of specimens immersed in 42°C, 50 vol % ferric chloride solution after 60 days exposure is presented in Figure 8. As observed, although the pure HDPE acts as a good coating, HDPE containing 0.5 wt % heat stabilizer behaves much better. Thus, after 60 days exposure, no destructive effect—such as peeling, cracking, blistering of coatings, or degradation of the polymer—was observed.

Visual and SEM examination of coated specimens subjected to salt spray tests for 700 h showed that HDPE coatings containing stabilizer were completely unaffected (Fig. 9), and no sign of any defect was observed. Conversely, peeling of pure HDPE coating from metal substrate surface

Figure 9 SEM micrograph showing HDPE coating with stabilizer on the substrate after 702 h exposure to salt spray.

was observed within the period of experiments. It is believed that this could be due to degradation of HDPE molecules, especially during the secondary curing process. Addition of 0.5 wt % stabilizer to HDPE can prevent this event. The infrared spectra of these samples confirm the effect of stabilizer. Performing ductility and adhesion tests on the preexposure specimens coated with HDPE containing heat stabilizer revealed no loss in the previously described properties due to immersion tests in various solutions and within the periods of time examined.

On the whole, it can be concluded that, if proper surface treatment is performed along with optimum curing time and temperature, HDPE containing heat stabilizer can be used as a good protective coating in corrosive environment, such as sulfuric acid and ferric chloride solutions. This is true for wet and humid atmospheres as well. While continuous subjecting to salt spray for 1000 h is equal to 15 years exposure in a humid atmosphere, HDPE containing stabilizer can be a good and effective coating in this condition as well.[20]

CONCLUSIONS

From the results presented in this article, the following conclusions can be drawn:

1. Using the electrostatic powder spray system and subsequent controlled curing treatment, good quality HDPE coating can be produced on plain carbon steel substrates.
2. Adhesion and ductility of HDPE coating on steel substrates are a function of surface preparation and roughness. The optimum condition was found to be when specimens were polished on 100 grit size sandpaper.
3. Adhesion and ductility of HDPE coating on steel substrates are a function of curing time and temperature. Optimum time and temperature were found to be 45 min and 220°C for pure HDPE coating and 45 min and 230°C for HDPE coating with 0.5 wt % stabilizer.
4. Adhesion and ductility of HDPE coating with 0.5 wt % heat stabilizer on steel substrate are more than without stabilizer.
5. The presence of a zinc phosphate prelayer would increase the adhesion and ductility

of HDPE coating on steel substrates to some extent.
6. HDPE can be an effective and protective coating for steel substrates in corrosive environments, such as sulfuric acid, ferric chloride solutions, humid atmospheres, and offshore environments.

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