Maleic acid grafted low density polyethylene for thermally sprayable anticorrosive coatings

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Abstract

Low density polyethylene (LDPE) coatings are being used in an ever growing range of applications. However, non-polar characteristics of LDPE make its adhesion poor to metal substrate and so become less suitable for anticorrosive coating application. An anticorrosive coating can therefore be developed if LDPE is modified with requisite polar groups. In the present work, a polar group has been introduced in polyethylene matrix by grafting maleic acid. Grafted LDPE was characterized by chemical method, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA), melt flow index (MFI), particle size analysis and hot stage optical microscopy. The presence of carbonyl peak of high intensity, high acid value and low melt flow index value confirmed grafting of maleic acid on LDPE. Change in crystallization behaviour of LDPE has been noticed after grafting. Grafted LDPE was applied on grit blasted mild steel surface by flame spray technique and adhesion study showed improved adhesion of grafted LDPE than LDPE. The coated panels were evaluated for resistance to corrosion in salt spray, humidity cabinet and seawater. The corrosion resistance of modified LDPE was also studied by AC Impedance technique. Grafted LDPE showed satisfactory corrosion resistance. Grafted LDPE was pigmented with red iron oxide and pigmented composition has shown improved resistance to corrosion in laboratory tests.

Keywords: Low density polyethylene; Radiation; Grafting; Flame spray; Adhesion; Corrosion resistance

1. Introduction

Protective coatings are employed to protect steel structures from corrosion due to exposure in marine atmosphere, such as salt spray, high humidity, ultraviolet radiation and other weather conditions. These coatings function by providing a barrier between the surface and corrosion inducing elements. Key attributes in the performance of protective coatings are, therefore, good adhesion to substrate, a low permeability to ions, water, gases and other corrosive species of the service environment. Factors that influence the choice of a coating system include the forms of corrosion encountered, exposure conditions and type of structure to be protected [1].

Protective coatings are generally formed on substrate by application of liquid paint at ambient temperature. During the drying process, solvents are released from such coatings which pollute the environment. Hence, it would be worthwhile considering a coating system which does not utilize solvents. One of the examples of such type of coatings is thermally sprayable organic coatings, which have attracted attention of corrosion engineers in view of several advantages [2]. Thermally sprayable organic coatings are thermoplastic in nature and they are 100% solid materials. Application of these coatings does not result in release of volatile organic compounds. These coatings form tough and firmly adherent barrier coatings. Film formation of these materials is virtually instantaneous, unlike other coatings, which may require several hours or even days to become suitable for service. Further more, they may also be applied at relatively low ambient temperatures. Since, these coatings are thermoplastic, they can be repaired easily in situ by remelting or applying additional material. Thermally sprayable organic coatings can have excellent chemical resistance depending on polymer type. These coatings are generally resistant to damage caused by impact and abrasion [3].

Thermally sprayable organic coatings are formed by thermally induced liquification of polymer powders and subsequent deposition on a substrate where cooling and solidification occurs. Polymers may be thermally sprayed as powders by either
plasma or flame spray techniques. Plasma spray uses a hot ionized gas as thermal source, while flame spray process melts the polymer feed-stock in an oxygen-fuel gas flame. Both methods employ compressed air to atomize and propel the molten polymer to the substrate.

Polyethylene, polypropylene, fluoropolymers [4] and thermoplastic polystyres are some of the polymers which can be sprayed by thermal spray process and are expected to provide longer service life to marine structures. In our work, we have selected low density polyethylene (LDPE) as candidate material for thermal spray application because of its low cost and a wide range of physical and chemical properties.

Polyethylenes are of high commercial interest due to their wide range of physical and chemical properties. However, their use in polymer blends of technological interest has been limited due to their typical non-polar character leading to poor adhesion. To overcome this deficiency and to facilitate compatibilization with polar polymers, polyethylenes have been chemically modified through functionalization or grafting. This process introduces polar groups onto the polymer main chain as pendant units or short-chain branching [5]. It can be achieved by copolymerization of new monomers or by modification or blending of existing polymers [6].

Grafting of preformed polymer is an important method for preparation of polymers with suitable functional groups [7]. Grafting involves covalent coupling of species, usually monomers or chain extenders, onto an existing polymer backbone. Reactive sites for grafting can be generated by mechanical processing, by chemical initiation, by photochemical activation (UV-radiation) and by high-energy radiation (electron beam or gamma radiation). Grafting processes may be carried out under simultaneous treatment conditions, with all components being present during the creation of reactive sites. Alternatively, grafting can be performed via pre-activation grafting processes. Reactive sites are generated in the absence of the modifying species, but subsequently exposed to modifying species under some predetermed and controlled condition [8]. Recently, other methods have been developed such as atom transfer radical polymerization [9,10] or “living” radical polymerization [11,12]. These methods allow in controlling the length of grafts since they act more efficiently on the kinetics of the chain growth.

Maleic anhydride (MAH) is one of the widely used vinyl monomers for graft modification of polyolefins. It has been grafted to polyethylene by mechanical, free radical, ionic and radiation techniques [13]. The reason for use of maleic anhydride as monomer for graft modification can be attributed to chemical reactivity of the anhydride functionality. Rangnathan et al. [14] reported that performance of maleic anhydride graft modified polymers in adhesion and compatibilization can be expected to depend on the chemical nature and microstructure of the graft. Gaylord et al. [15–17] reported formation of single and oligomeric grafts during grafting of maleic anhydride onto polyolefins. In addition to these grafts, bridges consisting of single and oligomeric maleic anhydride units between polymer chains were proposed. Formation of free poly(maleic anhydride) was also observed, which could be reduced by using additives that suppressed formation of homopolyner.

Considerable studies have been carried out on maleic anhydride [13–18] grafting of polyethylene. But authors have not come across any reported work where maleic acid (MAc) has been taken as starting material for grafting on low density polyethylene (LDPE). Maleic acid has been reported [19] to improve adhesion of coating due to its high polarity. The aim of the present work is to introduce polar groups in polyethylene matrix by grafting maleic acid using γ-radiation to improve the adhesion of LDPE to metal surface and use the modified LDPE for development of thermally sprayable organic coating for marine environment.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) powder obtained from IPCL (India), has a density of 0.93 g/cm³, average particle size of 267 μm and melting point of 103°C. LDPE powder was sieved in laboratory and powder having particle size less than 200 μm was used for grafting. MAc monomer used in the study, having 99.5% purity and melting point 136-141°C, was supplied by S.D. Fine Chem (India) and was used as received. Chemical reagents used for titration were of AR grade. Red iron oxide pigment was obtained from ZIGMA International (India).

2.2. Grafting of MAc on LDPE

Hundred grams of LDPE powder of less than 200 μm particle size was exposed under atmospheric conditions at different levels of radiation in a γ-radiation chamber using Co-60 as source. Immediately after irradiation, powder was transferred to a three-necked flask containing 350 ml aq. MAc solution (10%, w/v). The reaction mixture was maintained at 80–90°C for 3.5 h under nitrogen atmosphere. Irradiated powders were agitated continuously by using a magnetic stirrer. After completion of reaction, the powder was separated by filtration, transferred to hot distilled water and stirred for about 30 min and filtered. The powder was washed thoroughly with hot water to remove any free maleic acid. Grafted LDPE powder (LDPE-g-MAc) was dried under reduced pressure at 80°C for 16 h before characterization.

2.3. Pigmentation of LDPE and grafted LDPE

Red iron oxide was used for pigmentation of LDPE and grafted LDPE. A blend of red iron oxide and resin, in 1:4 ratio, was prepared by extrusion method. The blend was extruded at 140°C in single screw extruder at 50 RPM for 10 min. After extrusion, blend was passed through a cryogrinder to achieve required particle size, suitable for thermal spray application.

2.4. Characterization

2.4.1. Acid value and percent grafting

Acid value and percent grafting were determined by titrating grafted product. 0.5 g of grafted sample was suspended in 25 ml of 0.1N NaOH solution (aq.). Reaction mixture was stirred for
2.4.2. Melt flow index
Melt flow index measurements were carried out as per ASTM D-1238, using Tinius Olsen meltflow Indexer (Model MP600). As melting points of LDPE and LDPE-g-MAc are 103 and 105 °C, respectively, measurements were carried out at 113 °C.

2.4.3. Infrared spectroscopy
LDPE and grafted LDPE samples were converted into thin films by hot pressing at 130 °C and were directly mounted on the frame of spectrophotometer. FTIR spectra of films having identical thickness were recorded by employing a Perkin-Elmer spectrophotometer (Model 1600 series). The FTIR spectrum of grafted LDPE was also taken after application by flame spray.

2.4.4. Thermal properties
Melt of polymeric powders were determined by using a differential scanning calorimeter (TA Instruments, Model Q 100). DSC measurement was carried out with a ramp of 10 °C/min maintained during heating scan under nitrogen atmosphere. Cooling scan was performed at a rate of 1 °C/min after holding the sample at 110 °C for 30 min. Thermal decomposition temperature was studied by thermo-gravimetric analyser (TA Instruments, Model Hi-Res. TGA 2950) at a heating rate of 10 °C/min under nitrogen atmosphere to a temperature of 800 °C.

2.4.5. Particle size analysis
Particle size analysis was carried out on Mastersizer-2000 of Malvern Instruments by dispersing small quantity of powder in aqueous and non-aqueous medium in presence of dispersing agent.

2.4.6. Hot stage microscopy
Crystallization behaviour of LDPE and LDPE-g-MAc was studied by taking optical micrographs on a Hot stage microscope (Leica Model DMLD). In this experiment, samples were heated from room temperature to 130 °C at a heating rate of 20 °C/min to get clear melt. Cooling scan was performed at a rate of 5 °C/min after holding the sample at 130 °C for 2 min. Cooling was continued till a temperature of 107 °C and the sample was maintained at this temperature for 10 min to facilitate the crystal growth. After this temperature no change in crystallization was observed.

2.4.7. Thermal spray application
LDPE, LDPE-g-MAc and pigmented compositions were applied on grit blasted mild steel surface by flame spray method directly to avoid additional step of hydrolysis of MAN to MAc as done in conventional methods [11–16]. LDPE-g-MAc, thus obtained was characterized by various techniques.

3. Results and discussion
Irradiation generate free radicals in LDPE powders [8,20]. Some of the radicals present in powders participate in grafting on LDPE. In this study, an attempt was made to graft MAc directly to avoid additional step of hydrolysis of MAN to MAc as done in conventional methods [11–16]. LDPE-g-MAc, thus obtained was characterized by various techniques.

Table 1 shows variation in percent grafting at different radiation doses. As expected, extent of grafting increased with radiation dose. Maximum grafting of 2.4 wt.% was observed for 60 kGy dose.
Fig. 1 shows FTIR spectra of LDPE under different conditions. Grafting of MAc is expected to result in the presence of carboxylic group and hence, the peak corresponding to this group expected to appear at 1714 cm\(^{-1}\) in the FTIR spectrum. Spectrum corresponding to LDPE has a very small peak at 1714 cm\(^{-1}\). Irradiated LDPE (spectrum b) and LDPE-g-MAc (spectrum c) exhibit sharp peaks at 1714 cm\(^{-1}\) indicating presence of carboxyl group. However, intensity of peak for LDPE-g-MAc is higher compared to that of irradiated LDPE. It has been reported in literature\(^{[21]}\) that exposure of LDPE to \(\gamma\)-radiation in air leads to formation of carbonyl groups due to oxidation. To ascertain the observation that peak appearing at 1714 cm\(^{-1}\) in spectrum of LDPE-g-MAc is due to grafting of MAc, acid values of LDPE and LDPE-g-MAc were determined. Acid value (AV) and percent grafting were calculated using following equations:

\[
\text{Acid value (AV)} = \frac{56.1 \times (V_b - V_s) \times N_{\text{HCl}}}{W} \quad (1)
\]

where \(V_b\) is the titre value for blank, ml; \(V_s\) the titre value for sample, ml; \(N_{\text{HCl}}\) the normality of hydrochloric acid; \(W\) is the weight of the sample.

\[
\text{Percent grafting} = \frac{E_{\text{MAc}} - E_g}{E_g} \times 100 \quad (2)
\]

where \(E_{\text{MAc}}\) is the equivalent weight of maleic acid and \(E_g\) is the equivalent weight of grafted LDPE.

Higher acid value of LDPE-g-MAc (Table 2) compared to LDPE indicated grafting of MAc onto LDPE. The grafting of MAc to LDPE is further established by melt flow index results, shown in Table 2. It is expected that introduction of polar group in LDPE matrix will lead to reduction in melt flow index due to hydrogen bonding.

Fig. 2 shows FTIR spectrum of LDPE-g-MAc before and after flame spray application. In both the cases, carboxyl group peak appears at 1714 cm\(^{-1}\) which indicates that LDPE-g-MAc has retained carboxyl groups even after application by flame spray.

DSC curves in Fig. 3 show melting points of unexposed LDPE, irradiated LDPE, and LDPE-g-MAc at 103, 103.5 and 105°C, respectively. This change in melting point after grafting can be attributed to the presence of polar carboxyl groups. However, the effect is small as the grafting level is very low. Exposure to \(\gamma\)-radiation does not affect the melting point and crystallization temperature of LDPE. Cooling thermogram shows crystallization peak for LDPE at 99°C, whereas for LDPE-g-MAc, peak appeared at 97°C. The downward shift of crystallization peak for LDPE-g-MAc can be attributed to hindrance by the polar groups generated by grafting of MAc. Fig. 4 gives TGA thermograms of LDPE and LDPE-g-MAc. Decomposition of LDPE and LDPE-g-MAc is seen to start at 410°C showing that the degradation behaviour of LDPE has not changed due to grafting. Low grafting is not expected to change much of the thermal degradation behaviour. The large difference between the melting (i.e., 105°C) and degradation temperatures (i.e., 410°C) of LDPE-g-MAc makes this resin suitable for flame spray application.

Particle size analysis carried out in aqueous medium shows a marginal increase in the size of LDPE from 187 to 192 µm due to grafting. This increase in particle size was not observed.
when analysis was carried out in non-aqueous medium. Hence, this increase in particle size is mainly due to the swelling of the grafted material in aqueous medium assisted by the polar COOH group.

The extent of crystallization of LDPE and LDPE-g-MAc can be seen in optical micrographs presented in Fig. 5 (a and b), respectively. Samples were annealed at temperature above melting point before commencing cooling scan. Slow cooling enabled crystallization of both samples. It can be seen that at 107°C the crystal growth in LDPE sample is quite prominent and crystal size is also found to be large. In case of LDPE-g-MAc, crystal growth occurs at this temperature but the crystal size is smaller compared to that seen in LDPE. This may be due to a reduced stacking in case of LDPE-g-MAc. It is obvious that presence of MAc can introduce hydrogen bonding in grafted LDPE and due to this reason only fine crystals resulted.

Fig. 6 shows the adhesion strength of flame sprayed LDPE, grafted LDPE, red oxide pigmented LDPE and grafted LDPE. It is seen that grafting with maleic acid enhances adhesion of LDPE to mild steel surface due to introduction of polar groups in the polymer matrix. Pigmentation with red iron oxide does not affect the adhesion strength of LDPE but a slight decrease in the adhesion strength in the case of grafted LDPE has occurred. The decrease in adhesion strength is possibly due to adsorption of some of the polar groups from maleic acid grafted LDPE on red iron oxide surface and hence less number of polar group were available for interaction with substrate.

Grit blasted mild steel panels coated with LDPE, LDPE-g-MAc, red iron oxide pigmented LDPE and LDPE-g-MAc were exposed to salt spray, humidity cabinet and seawater for 13 weeks to evaluate their resistance to corrosion. The results are given in Table 3. It is evident from the results that the grafted LDPE exhibit higher resistance to corrosion as compared to ungrafted LDPE under all exposure conditions. The onset of corrosion in LDPE was noticed after 3 weeks of exposure and it increased with time, whereas in case of LDPE-g-MAc, first corrosion spot was observed after 11 weeks of exposure. Results shown in Table 3 indicate that pigmentation improved the corrosion resistance of these two resins. Improved corrosion re-
Fig. 7 shows the change in coating resistance of LDPE and LDPE-g-MAc with time. At the initial stages of experiment, both polymers possess high resistance and after 30 days LDPE showed a sharp drop in resistance and after 50 days of exposure resistance has further dropped down and it has gone below the allowable level (i.e., less than $10^6 \, \Omega \cdot \text{cm}^2$) [22]. Though, LDPE is hydrophobic in nature, the poor adhesion of LDPE to metal surface may be one of the reasons for onset of corrosion. In the case of LDPE-g-MAc, a drop in coating resistance was noticed after 50 days, but its resistance remained higher than allowable level even after 75 days of exposure. It is evident from Fig. 8(a) and (b) that both the coatings are porous but the pores in LDPE-g-MAc are lesser in number and small in size than LDPE. This may be the reason for improvement in resistance to corrosion of LDPE-g-MAc. The EIS results are also in agreement with the results obtained by accelerated exposure tests (Table 3), where LDPE-g-MAc has shown better resistance to corrosion than LDPE.

4. Conclusion

Maleic acid was grafted to LDPE by pre-activation method using γ-radiation. The dose was varied to achieve different level of grafting. Maximum grafting of 2.4% was achieved at 60 kGy dose. Grafted LDPE has shown modified properties compared to LDPE. FTIR has shown generation of carboxyl group in grafted LDPE which led to an acid value of 23. Grafting has not affected thermal and mechanical properties of LDPE to appreciable extent. However, a noticeable change in crystallization behaviour has been observed after grafting. Reduced crystalline growth of grafted mass was observed in optical microscope. Grafted LDPE has shown improved corrosion resistance compared to LDPE resin. Pigmentation with red iron oxide has further improved the corrosion resistance of LDPE-g-MAc.

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