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Ethylene vinyl acetate and ethylene vinyl alcohol copolymer for thermal spray coating application

S.P. Tambe, S.K. Singh, M. Patri, Dhirendra Kumar*

Naval Materials Research Laboratory, Shil-Badlapur Road, P.O. Anandnagar, Ambernath 421506, India

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ABSTRACT

Ethylene vinyl acetate (EVA) copolymer with varying vinyl acetate (VAc) content, viz. 18%, 28% and 40% has been hydrolyzed using alcoholic NaOH solution. Fourier Transform Infrared Spectroscopy (FTIR) analyses of hydrolyzed polymer showed the presence of both OH group and acetate group indicating that the EVA has been partially hydrolyzed. Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analyzer (TGA) of EVA and hydrolyzed EVA showed large difference in melting and decomposition temperature, respectively. Hydrolyzed EVA showed higher tensile strength and elongation at break compared to corresponding EVA. Blends of different grades of EVA and ethylene vinyl alcohol (EVAl) with low density polyethylene (LDPE) were applied on grit blasted mild steel surface by flame spray technique. FTIR analysis of blends before and after coating showed no degradation during flame spray. Measurement of adhesion strength of these coating showed that adhesion strength increased on hydrolysis of EVA.

1. Introduction

Environmental and health concerns have brought in major restrictions on the use of solvent-based coatings. This has led to changes in composition, surface preparation procedures, and application techniques. Traditional solvent-borne coatings, such as alkyds and epoxies, have been reformulated to meet the volatile organic component (VOC) regulations [1] by using binders possessing lower viscosities or using other techniques to lower the VOC content.

Thermally sprayable organic coatings are 100% solids without requirements of post application treatment for film formation and curing processes as done in case of powder coatings. In such coatings, film formation takes place by deposition of molten polymeric mass on the substrate. It is a single coat process and is ideally suited for large structures. Maintenance of these coatings is simpler as it can easily be repaired by in situ remelting or by additional coating at desired locations. Since, application of this coating does not involve release of VOC, it can be safely used in interior compartments of ships and other structures where ventilation is a problem.

Another advantage of using this technique is that polymers, which are known to provide good anticorrosive property but cannot be applied on the surface by dissolving in common solvents, can be deposited on the surface in the molten form. The major critical parameter of this application technique is to control the powder flow rate since application process is carried out between melting and decomposition temperatures. However, there must be wide difference between the melting point and decomposition temperature of the polymer. Polyethylene (PE), polyamide, polyester and their blends are among most commonly used thermoplastic materials for flame and plasma spraying [2–9].

Polyethylene is most commonly used for many applications due to its wide range of physical and chemical resistance properties. However, adhesion of PE onto metal substrate is poor due to its non-polar characteristics. Considerable work has been carried out in our laboratory on the modification of low density polyethylene and its subsequent use as coating materials for thermal spray application [10–12]. LDPE has been modified by grafting maleic acid both by irradiation and extrusion techniques. Thermal spray coating of grafted material and their pigmented compositions have shown improved adhesion strength as well as anticorrosive property.

Ethylene vinyl acetate (EVA) copolymer, another commercially available thermoplastic has broad industrial applications, ranging from hot melt adhesive to wine bottle closures and cable sheathing. EVA is commercially available with vinyl acetate (VAc) content varying from 3 to 50%. The properties of EVA vary with VAc content. It is reported that [13] VAc content up to 10% is more transparent, flexible and tougher than LDPE. Between 15 and 30% VAc content copolymers are soft and flexible. Compounds with 30–40% VAc are soft, elastic and their strength and adhesion properties are desirable for coatings and adhesives. Between 40 and 50% VAc in EVA has rubber like properties. The acetate group being bulky prevents adjacent PE packing into crystal lattices, therefore EVA copolymer with VAc content more than 30% (w/w) is amorphous in nature.

* Corresponding author. Tel.: +91 251 2620187; fax: +91 251 2620604.
E-mail address: dhikumar@rediffmail.com (D. Kumar).

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Table 1
Characteristics of EVA copolymers used for the study

Polymer	Vinyl acetate (% w/w)	Melt flow index (g/10 min)	Density g/cc
E1	18	2.5	0.96
E2	28	3	0.95
E3	40	41	0.93

Ethylene vinyl alcohol (EVAl) copolymer, prepared by hydrolysis of EVA, is one of the most impermeable polymer [14]. EVAl copolymer consists of hydrophilic vinyl alcohol and hydrophobic ethylene parts. During hydrolysis of EVA, acetate group is converted into hydroxyl group leading to change in thermal, physical and mechanical properties of EVA.

However, no study is available in literature on the application of EVAl by thermal spray coating. In the present work, EVA has been hydrolyzed and both EVA and EVAl have been characterized for structure and mechanical properties. Blends of LDPE/EVA and LDPE/EVAl have been applied on mild steel surface by thermal spray coating technique and evaluated for adhesion strength.

2. Experimental

2.1. Materials

EVA copolymer in granular form was obtained from two sources: EVA copolymer (18% VAc) from Reliance (India) Ltd., whereas EVA copolymers (28% and 40% VAc) from Du Pont Ltd. (USA). The properties of different grades of EVA are given in Table 1. Low density polyethylene (LDPE) in powder form was obtained from IPCL (India), and has a density of 0.930 g/cm^3, average particle size 263 μm and melting point 103 °C. Sodium hydroxide and tetrahydrofuran (AR grade) was obtained from S.D. Fine Chem. (India). Chemical reagents used for titration were of AR grade.

2.2. Hydrolysis of EVA

Hydrolysis of different grades of EVA (E1, E2 and E3) copolymer was carried out as per procedure reported by Hirata et al. [15]. The reaction was carried out in three-necked round bottom flask equipped with reflux condenser and stirrer. In a typical process, 50 gm of EVA was dissolved in 250 ml of tetrahydrofuran. To the reaction mixture, measured volume of 0.5 M alcoholic NaOH was added; 65 ml in the case of E1 and E2 whereas 80 ml in the case of E3. The reaction mixture was refluxed under nitrogen atmosphere for different time intervals, i.e. 1, 2 and 3 h. After completion of the reaction, the medium was neutralized by 1 N HCl solution. The reaction mass was then precipitated in chilled distilled water. The precipitate was washed repeatedly using distilled water to remove inorganic salt and dried at 80 °C under reduced pressure till constant weight (approximately 10 h).

2.3. Hydroxyl value determination

Hydroxyl value of hydrolyzed EVA was determined by the following method.

1 gm of hydrolyzed product was dissolved in 25 ml of toluene. 5 ml of acetylating mixture, obtained by mixing acetic anhydride and distilled pyridine at a ratio of 70:30 (w/w) was added to the reaction mixture and the content was refluxed for 24 h. Afterwards, 5 ml of water was added through condenser and heating was continued for 10 min. Reaction mixture was allowed to cool and the condenser was washed with 15 ml of *n*-butanol. Unreacted acetic anhydride was determined by titrating with standard (approximately 0.5 N) alcoholic KOH solution using phenolphthalein indicator. The OH value determination was carried out in duplicate. Similar experiment was carried out for blank.

$$\text{Hydroxyl value}\,(A) = \frac{(B - S) \times 56.1 \times N}{W} \quad (1)$$

where B is the volume of KOH in ml consumed for blank; S is the volume of KOH in ml consumed for sample; N is the normality of KOH solution; W is the weight of the sample in g.

Theoretical hydroxyl value of hydrolyzed EVA (for example 18%VA) was calculated as follows.

Equivalent weight of vinyl alcohol = 44 gm
Since 18% vinyl alcohol is present in fully hydrolyzed EVA (18% VA) The OH equivalent weight = 244 gm. Then theoretical hydroxyl value (T)

$$\text{Hydroxyl value}\,(T) = \frac{56.1 \times 1000}{-\text{OH equivalent}} \quad (2)$$

The extent of reaction also known as degree of hydrolysis (DOH) was calculated by substituting the values of T and A in Eq. (3),

$$\text{DOH} = \frac{A \times 100}{T} \quad (3)$$

3. Characterization

3.1. Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy

Different grades of EVA copolymers and corresponding hydrolyzed EVA copolymer powders were converted into thin film by hot pressing at 150 °C. FTIR spectra of film having similar thickness were recorded using spectrophotometer (Thermo Electronic Corporation, Model-NICOLET-5700). The spectra were recorded in the 400–4000 cm^{-1} range with a resolution of 4 cm^{-1} and 16 scans per spectrum.

3.2. Thermal analysis

Melting temperature of EVA and hydrolyzed product was determined by using a Differential Scanning Calorimeter (DSC) (TA Instruments, Model-Q100). Measurements were carried out at a heating rate of 10 °C/min under nitrogen atmosphere. Thermal stability of EVA and EVAl copolymer was studied by Thermo Gravimetric Analyzer (TGA) (TA Instruments, Model-Hi-Res. TGA 2950) at a heating rate of 10 °C/min under nitrogen atmosphere up to 800 °C.

3.3. Mechanical properties

Tensile strength and elongation at break of different grades of EVA, EVAl copolymer films were measured using Universal Testing Machine (LLOYD, Model-LR30K) as per procedure described in ASTM-D838. The test specimens were prepared by compression molding at 150 °C and were allowed to cool at room temperature. Free films having an average thickness of 200 μm were strained at a rate of 20 mm/min. Average result of five highest readings at peak load has been reported as tensile strength.

3.4. Blending of LDPE with EVA and EVAl

Different grades of EVA and EVAl (maximum DOH of each grade of EVA) named as E1, E2, E3, Ea1, Ea2 and Ea3 in Table 2, copolymers were blended with LDPE separately at 50:50 w/w ratios. The blends were mixed at 170 °C in an internal mixer (Brabender Plasticorder) at 50 rpm for 7 min. After mixing, blends were passed through a