ABSTRACT
Historically, coatings for steel structures such as paints and primers were applied as protective barriers against corrosion. To meet the current challenges of an aging infrastructure, protective coatings must not only provide adequate corrosion protection but should also offer mechanical strengthening whether via arresting crack propagation or redistributing stresses brought about through welding, cutting or corrosion damage. A novel thermoplastic polymer blend consisting of additions of the DuPont™ polymer Elvaloy® to high density polyethylene (HDPE) was developed and characterized for applications as a protective coating and as a fiber reinforced composite for strengthening and rehabilitation of steel. Elvaloy is an ethylene terpolymer containing epoxy functional groups based on a glycidyl methacrylate (GMA) component. The incorporation of Elvaloy to HDPE was found to lower tensile strength while increasing strain-to-failure. The proposed system may be implemented as a protective coating for steel at low Elvaloy loading (25-33 wt%). These compositions showed the greatest adhesive performance along with high tensile strength and strain-to-failure. Similarly, when using the polymer blend as a matrix material for carbon fiber-reinforced composite materials, low Elvaloy loading (25-33 wt%) shows promise for retrofit and rehabilitation applications. The reversible curing cycle of the thermoplastic blends make them an attractive material for quick in-the-field bonding with minimal curing time.

INTRODUCTION
The demand for protective coatings for corrosion control of metal structures is continually important in the transportation and marine industries. Appropriate coatings for steel must be tough, abrasion resistant, impermeable to attack from moisture and chemicals, easily applied in-situ and of course highly adhesive to the substrate to be protected [1]. The use of thermoplastic polymer materials is gaining acceptance over thermosetting materials for such applications due to the ability for quick in-the-field bonding [2] using a variety of fusion bonding methods [3]. Hot-melt thermoplastics eliminate the need for harmful solvents which reduce production (drying) time and offer a more environmentally friendly approach with reduced emissions [4,5]. Additionally, thermoplastic coatings may be applied in various thicknesses, whereas thermoset epoxies must be applied in thin, often brittle layers. Perhaps the most commonly used thermoplastic in such applications is polyethylene [6]. However, the implementation of polyethylene is limited by poor adhesive properties. It has been suggested that blending
polyethylene with polar polymers may help increase dry adhesion between polymer coatings and high surface energy steel substrates [7].

New material coating systems must not only provide the necessary corrosion protection, but should also maintain the integrity of the structure via arresting crack propagation of corrosion weakened sections and joints [8]. Additionally, these systems could assist in rehabilitation of steel components damaged through seismic events or which are deficient due to cracks and/or other defects and their progression. Fiber reinforced thermoplastic coatings may help redistribute stress built up as a result of corrosion damage or even residual stresses brought about through application of heat as in welding or cutting. Making use of the reversible curing cycle of thermoplastic matrix materials may reduce costs through labor savings and the elimination of service disruption for repairs associated with thermosetting coatings.

Historically, high adhesive strength has been best established by coatings in the family of ethylene copolymer ionomers, which are neutralized ethylene methacrylic acid copolymers. These materials possess the desired toughness, impact resistance and adhesion but are sensitive to the diffusion of moisture at high temperatures. An olefin (polyethylene) system seems like a better choice for such coating applications. Recent ethylene/n-butyl acrylate/glycidyl methacrylate formulations (Elvaloy® 4170 by DuPont™), taking advantage of an epoxy functionality in the GMA component, show promise for novel coating systems; however they are too soft and pliable to be implemented independently. The objective of this work was to blend the thermoplastic resin modifier; DuPont’s Elvaloy, with high density polyethylene (HDPE) in various compositions and characterize the mechanical and thermal properties as well as the adhesive performance when bonded to structural steel. The application of HDPE/Elvaloy blends as matrix materials for carbon fiber reinforced thermoplastic composites is also considered for rehabilitation and retrofit coatings of steel structures.

**EXPERIMENTAL**

**Materials**

High density polyethylene (HDPE) resin produced by Scientific Polymer Products (MFI = 1 g/10min; $M_w = 125,000$) was compounded with DuPont’s Elvaloy resin modifier (MFI = 12 g/10min). The terpolymer contains an ethylene backbone with $n$-butyl acrylate, an elastomeric toughening agent, and glycidyl methacrylate, a dual functionality epoxidized adhesion promoter. Carbon fibers used in composite manufacture were of a biaxial weave. Steel substrates used for lap shear adhesion testing are A36 hot-rolled steel coupons with dimensions of 25.4 mm x 101.6 mm and thickness 1.53 mm.

Two surface pretreatments techniques were performed on steel substrates. *Polished* surfaces were achieved using 320-grit silicon carbide paper and a rotary polishing wheel. *Sand-blasted* surfaces were achieved using 320 grit roughening media. A silane coupling agent was also employed in several adhesive measurements. Gamma-aminopropyltriethoxysilane, produced by Aldrich™, was selected based upon its reactivity with the epoxide functionality of the GMA component of Elvaloy. Two concentrations of silane (3% and 10%) in a methanol/ethanol solution were produced to achieve varying silane layer thicknesses on steel. While more sophisticated surface pretreatment techniques such as laser roughening and corona discharge
could be employed to maximize adhesive performance, they were not considered in this work as they prove to be impractical for in-the-field applications.

**Polymer Fabrication and Composite Manufacture**

A reciprocating screw injection molder was used to prepare polymer blends of varying compositions. Elvaloy (HDPE 0/100) was added to HDPE (HDPE 100/0) at: 25, 33, 50, 66, and 75 wt% (HDPE 75/25; HDPE 66/33; HDPE 50/50; HDPE 33/66; HDPE 25/75, respectively) additions. Elvaloy was dried overnight at 60°C prior to injection molding to remove absorbed moisture. After a lengthy trial study, the following injection molding conditions gave uniform specimens for all polymer blends: three heat zones at a constant 190°C with the mold heated to 40°C to minimize coupon shrinkage. Tensile “dog bones” were molded to specifications listed in ASTM D638. Moldings of thin rectangular polymer strips were used for carbon fiber impregnation. Fabric impregnation was done using a hot-plate compression molder. The thin polymer layer was placed over the fiber weave and pressed at 1 MPa for 1 min at 225°C. Impregnated fiber plies were then hot pressed under the same conditions to build up a 4-ply laminate of approximate thickness 1.53 mm. The 4-ply laminate is representative of a pre-fabricated panel which could be hot-melt bonded to steel using a variety of bonding techniques. A modest fiber mass fraction, \( M_f \), of 30-40% was achieved.

**Tensile Testing**

Tensile testing was performed using a model 5583 Instron tensile tester according to ASTM D638. Sand paper was used in the machine grips to avoid pull-out and “slippage.” The extension rate was 50 mm·min\(^{-1}\) and all tests were performed at room temperature. Five samples were tested for each composition.

**Single-Lap Shear Adhesion Test**

Metal/metal joints were prepared using hot press molding. Steel coupons (A36) were cut to 25.4 mm x 101.6 mm and wiped clean with acetone prior to bonding. A polymer sample size of 0.55 mg was found to give the necessary amount of material to cover an adhesive area of 645.16 mm\(^2\) (1 in\(^2\)). The metal substrates were preheated prior to bonding. The polymer sample was then placed on the heated substrate and pressed for 1 min at 225°C with 1 MPa pressure for all blends. Dynamic scanning calorimetry data collected for each sample blend showed a minimal melting temperature depression from 129.7°C for HDPE 100/0 to 127.2°C for HDPE 25/75; each well below the temperature applied for hot-melt bonding (225°C). The effectiveness of surface pretreatments and the use of a silane coupling agent on adhesion between polymer and steel were also observed using this technique.

Single-lap shear joints were also prepared for bonding pre-fabricated composite strips to steel substrates. In this case, only the metal substrate was preheated and placed on the heated (bottom) platen. The upper platen remained at 18°C to eliminate melting and deformation of the composite strip. The adhesive performance of metal/metal and composite/metal joints was evaluated using a servo-hydraulic Instron tension testing machine. Sample joints were loaded to failure at 13 mm/min and maximum load recorded to find adhesive shear strength of the polymer series bonded to steel.
RESULTS

Tensile Testing

Tensile stress-strain relationships in Figure 1 show the physical effects of blending Elvaloy with pure HDPE. The ductile behavior in HDPE 100/0 is representative of the spherulitic morphology seen in semi-crystalline polymers. The addition of Elvaloy to HDPE greatly increases the extension-to-failure but decreases strength. Visual observations of the tensile fracture surface at HDPE 75/25 and HDPE 66/33 showed fibril failure. All other blends showed wedge mode failure characteristic of lamellar separation, shear, and slip in high density polyethylene [9,10]. The excessive formation of fibrils shows the usefulness of Elvaloy as a plasticizer at loading of 25-33 wt%. The plasticizing effect is seen in the step-wise strength drop and extension-to-failure curves characteristics of these blends (HDPE 75/25; HDPE 66/33) in Figure 1.

![Figure 1: Stress-Extension Curves for HDPE, Elvaloy, and Their Blends at a Displacement Rate of 50 mm/min.](image)

Single-Lap Shear Metal/Metal Joints

The adhesive properties of HDPE/Elvaloy blends were characterized between metallic substrates by lap-shear tensile testing. Figure 2 shows the adhesive performance of HDPE hot melts with the addition of Elvaloy. The shear strength adhesion measurements of HDPE/Elvaloy blends vary slightly with the incorporation of Elvaloy. A subtle peak in adhesive strength between metallic substrates occurs at 33 wt% Elvaloy. This may be understood to be competing cohesive/adhesive properties within the polymer blend where HDPE provides strength and Elvaloy provides the functional groups necessary for interfacial adhesion. This is supported in visual observations of the failure surfaces. Pure adhesive failure is seen in HDPE 100/0 where the polymer is completely intact to one metal surface but there is no residual polymer bound to the other metal lap-shear coupon. However, as Elvaloy content increases, failure mode shifts to cohesive failure where both polymer/metal interfaces are intact and failure occurs in the polymer layer.
Effect of Surface/Silane Pretreatments
The lap-shear adhesive strength of HDPE 100/0, HDPE 66/33 and HDPE 0/100 samples was measured with the incorporation of two different surface pretreatments and a silane coupling agent at varying concentrations. Figure 3 shows the change in adhesive performance between polished (320-grit) and sand-blasted steel surfaces. In the case of HDPE 100/0, the adhesive mechanism of mechanical interlock is dominant in grit blasted steel surfaces as shown by the large increase in adhesive performance. However, in Elvaloy and the Elvaloy-containing blend, polished surfaces provided increased adhesion most likely due to optimized surface wetting associated with the high surface energy substrate.
The use of a silane coupling agent to promote adhesion between steel surfaces is shown in Figures 4 and 5. No significant deviation is seen in Elvaloy and Elvaloy-containing between a 3% and 10% silane agent. However, in the case of HDPE 100/0 with 10% silane treatment, optimized adhesion is seen in the grit-blasted condition. HDPE 66/33 in conjunction with the
3% silane coupling agent on polished steel substrates exhibits the highest adhesive strength of Elvaloy-containing blends, approximately 9 MPa.

**Single-Lap Shear Composite/Metal Joints**
The application of HDPE/Elvaloy blends as polymer matrix for composite materials eliminates the need for an external adhesive when bonding composite panels to steel, such as in rehabilitation and retrofit coatings. Adhesive performance of carbon fiber reinforced PE/Elvaloy composites is shown in Figure 6. Adhesion of HDPE to steel is enhanced with the integration of Elvaloy into the polymer blend. Much like the case of metal/metal joints (Figure 2), an apparent maximum adhesion is found at 33 wt% Elvaloy, although the increase is quite subtle. This is most likely due to the fibrilous failure of the blend and its high strength and strain to failure properties.

![Graph showing Adhesive Shear Strength vs. Elvaloy content](image)

**FIGURE 6: LAP SHEAR ADHESIVE STRENGTH OF FIBER REINFORCED COMPOSITES HOT MELT BONDED TO STEEL WITH VARYING CONTENT OF ELVALOY AS THE MATRIX MATERIAL.**

A continual shift in failure mode was observed from pure adhesive failure (HDPE 100/0) to complete cohesive failure (HDPE 25/75 and HDPE 0/100). Figure 7 shows the failure mode of composites hot melt bonded to steel. The observation that the steel coupon in Figure 7a is free of residual polymer, along with no deformation at the composite interface, identifies pure adhesive failure. At 33 wt% Elvaloy (Figure 7b) there is slight polymer tearing indicating mixed adhesive-cohesive failure. This is observation is intensified at 50 wt% Elvaloy (Figure 7c). Figures 7d and 7e show total cohesive failure as the two surfaces were separated between the carbon fiber plies.

This result indicates promise for these materials as possible rehabilitative coatings where higher quality manufactured composites (high fiber volume fraction) would yield thinner polymer layers and higher interlaminar strength. This is likely why the thin polymer layers in the metal/metal joints displayed higher adhesive strength.
FIGURE 7: TYPICAL FAILURE SURFACES OF COMPOSITES BONDED TO STEEL (A) HDPE 100/0; (B) HDPE 66/33; (C) HDPE 50/50; (D) HDPE 33/66; (E) HDPE 0/100. SCALE IN INCHES.

CONCLUSIONS
Compounding Elvaloy resin modifier into high density polyethylene alters the thermal, physical and adhesive properties of the pure resin. A near linear relationship shows the tensile strength of HDPE/Elvaloy blends decrease as Elvaloy is added to the blend. Overall, strain-to-failure is increased with Elvaloy content. The glycidyl methacrylate epoxide functionality of Elvaloy provides adhesion to metals. As Elvaloy was added to HDPE resin, adhesive properties increased only slightly in metal/metal joints at 33 wt% Elvaloy. Lower Elvaloy composition blends show better overall performance for coatings. As a result of this work, compounding lower additions of Elvaloy (25-33 wt%) will provide sufficient properties necessary for protective coatings of metals: high tensile strength (~13 MPa), a large strain-to-failure (300-400% extension) and increased adhesive properties when bonded to steel (8-10 MPa). The inclusion of Elvaloy in HDPE for composite matrix materials also shows promise for reinforced coatings with adhesive strength on the order of 2.5-4.5 MPa. Surface pretreatments of steel were shown to influence the degree of adhesion between HDPE, Elvaloy and their blends when bonded to steel. HDPE 66/33 polymer when used as an adhesive between polished steel substrates with 3% silane coupling agent, showed the highest adhesive strength of all the Elvaloy-containing blends.

Future work in this area involves durability testing of adhesive joints using the HDPE/Elvaloy blends and the application of carbon fiber reinforced thermoplastic composites for rehabilitation and corrosion protection for steel bridges and structures. This will enable rapid and cost-effective rehabilitation of structures while simultaneously enabling corrosion protection.
Furthermore, the ability to bridge cracks and redistribute stresses provides a critical tool for seismic retrofit.

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