ABSTRACT

Hybrid materials featuring thermoplastic polymer composites in conjunction with metals can be used as structural materials in commercial transport and military vehicles, and for protection of buildings and infrastructure. Constituent thermoplastics and metals have distinct advantages as protective materials, however metals on their own are heavy, hence hybrid materials offer option as lighter materials. This study focuses on the effect of surface treatments to improve adhesion between dissimilar materials such organic polymers with metal reinforcement materials. Surface energy was found to possess a direct relationship with the amount of polar groups on the surface of a modified polymer and free radicals on the metal surface. Higher surface energy correlates with superior interface adhesion. This work establishes the basis that polar groups and free radicals improve adhesion between polymeric (thermoplastics) and metallic surfaces.

INTRODUCTION

Thermoplastic composites are becoming more prevalent in automobile, aerospace, medical and electronic applications due to high-strength and low weight characteristics [1]. The growing demand for high performance thermoplastic-metal composites has been challenged by the problem of the lack of adhesion between fiber and matrix. Some of the adhesive mechanisms through which the surface treatments promote interfacial bonding include improvement of wettability, addition of chemical groups and variation of surface topography [2-8]. Previous research suggests that it is possible to improve the adhesive bonding between dissimilar materials across the interface [6-8].

This paper studies the effect of surface treatment to improve the adhesion of thermoplastic polymers to steel. Plasma treatment is used to provide reactive molecules (Si, H and C) on the surface of steel. Maleic anhydride (MA) is used to introduce carbonyl groups (–C=O) on polypropylene (PP) with a purpose to create reactive sites that promotes bonds between surfaces. Furthermore, this study analyzes the adhesion of steel to PP, soft and hard thermoplastic polyurethane (TPU) and polypropylene modified by maleic anhydride (PP-MA). The overall objective is to investigate mechanisms of bonding and finally enhance the bond at the interface between metal-polymer surfaces.
MATERIALS & METHODS

Materials: The thermoplastic polymers used were standard polypropylene (PP), Dow PM613 PP-MA, Merquinsa Pearlthane D11T75 and Pearlthane D11T85 TPU. The steel was a cold-rolled low carbon steel AISI/SAE 1018.

Contact Angle Test: Contact angle values were estimated by analyzing an image of a water droplet using a Reme Hart Goniometer (Model 100-00115) with a Sony CCD B/W digital camera module (model XCD-X700 with Dire-I 3.0 Software (9). For each material, five droplets of water on the surface were used to obtain the average of ten readings for each sample. A standard deviation less than 3 % was the higher limit to accept the value. Others parameters followed ASTM D5946 and ASTM D5725.

Lap Shear Strength Test: Lap shear strength tests were performed to analyze the effect of surface roughness, polymer type and metal surface treatment to the bond strength between metal and polymer. ASTM D3164M and D4896 were use to determine parameters and interpret results. ASTM D2093 and D2651 were used to prepare metal and polymer surfaces prior to the adhesion. The bond strength was calculated as the failure load divided by the fracture surface area. Six samples of each case were tested in tensile load with a Mechanical Testing System (MTS Systems Corp., Eden Prairie, MN, USA) under a displacement rate of 1.3 mm/s until failure. Steel specimens with optimized roughness were tested to bond with different polymers, PP, PP-MA, soft and hard TPU (10). Once the polymer with the highest bond strength was found, steel specimens with plasma treatment (Si-steel and C:H-steel) were tested to evaluate the metal surface modification.

Plasma Treatment on Steel Surface: Surface modification and coating was explored using a proprietary amorphous, hydrogenated carbon (a-C:H) coating vessel from Plasma Electronic, GmbH. The deposition method is Plasma Activated Chemical Vapor Deposition (PACVD). Under a controlled low atmosphere of reaction gases, the vessel induces a voltage bias of approximately 500 volts. The metal to be coated is put in contact with the cathode target, and uniform stable high energy plasma of reaction elements is formed on the entire cathode surface. The temperature of the process is 200ºC; in consequence no thermal impact is expected on the material.

RESULTS AND DISCUSSION

Molecular Characterization

Functional Polar Groups in Polymers: Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the composition of the thermoplastics used in the study. Because chemical bonds absorb infrared energy at specific frequencies (or wavelengths), specific functional groups of the polymer are determined by the spectral locations of their IR absorptions (peaks).

Figure 1 (left) compares the FTIR spectra of neat PP and PP-MA respectively. The spectra shows four absorption peaks at 2348, 1638, 997 and 675 cm⁻¹, the first and second peaks correspond to C=O carbonyl functional group, third to the C-O stretch anhydride functional group, and last to C-H bend alkene functional group. These groups constitute the MA. The MA content in PP-MA was calculated by Equation (1), where A₉₉₇ is the absorbance of the anhydride.
group at 997 cm$^{-1}$, $d$ is the thickness (mm) of the sample, and $K$ is a constant (= 0.25) detected by calibration of the known MA content of PP-MA.

$$\text{MA wt\%} = K \left( \frac{A_{997}}{d} \right) = 0.25 \left( \frac{0.07}{2} \right) = 0.875 \text{ wt \%} \quad (\text{Eq. 1})$$

Figure 1 (right) compares the FTIR spectra for two types of TPU, i.e. soft TPU and hard TPU. The -NH amide functional group is observed at 3298, 1528 and 1504 cm$^{-1}$; -C=O, carbonyl groups from ester are located at 1727 and 1698 cm$^{-1}$, functional carbons of aromatic rings –C=C are found at the range of 1600-1475 cm$^{-1}$ and the peak of isocyanate functional group –N=C=O is at 2341 cm$^{-1}$. All these peaks are active sites that are able to react with the steel surface due to the polarity and the double bonds. This explains the excellent adhesion of TPU to steel.

The intensity of the –CH alkane peaks and –C=O carbonyl peaks at 2919-2848 and 1727-1698 cm$^{-1}$ determines the amount of crystalline and amorphous regions in the polyurethane and generates the difference between soft TPU and hard TPU. For soft TPU, the higher content of amorphous regions correlates with the higher intensity of the peaks mentioned above.

**Contact Angle & Surface Energy:** Adhesion between surfaces is expected to proceed with the chemical attraction of specific sites. The contact angle was determined for different polymers and steel ‘with’ and ‘without’ coating treatment. Higher surface energy generates better adhesion to substrates with similar polarity. A contact angle equal to or greater than 80º signifies a hydrophobic surface. It is well known that polymers are hydrophobic and have low surface energies.

**Polymer Surfaces:** In general polymers have low surface energy with contact angles above 85º; a contact angle below this value is an indication that the polymer has been treated to improve adhesion. An angle close to 110º implies a hydrophobic behavior of the polymer, and an angle close to 70º is related to a hydrophilic polymer. Figure 2 shows typical optical measurements of contact angle for the polymers in the study. As predicted PP has high contact angle of 84º, followed by PPMA with 79º and soft TPU with 76º.

Figure 3 compares the results of surface energy and contact angle for PP, PP-MA and soft TPU. As expected PP has the lowest surface energy (35 dyne/cm) due to the saturated polymer
chain without any polar groups to react. Functionalization of PP is achieved by maleic anhydride to create -CO= reactive polar groups, these polar groups increase wettability of the polymer and consequently adhesion with the metal substrate.

![Figure 2. Droplets of distillated water on polymer surfaces for measuring contact angle](image)

**Figure 2.** Droplets of distillated water on polymer surfaces for measuring contact angle

![Figure 3. Contact angle and surface energy for different polymer types. Tall bars – Contact angle (degrees); Short bars – Surface energy (dyne/cm)](image)

**Figure 3.** Contact angle and surface energy for different polymer types. Tall bars – Contact angle (degrees); Short bars – Surface energy (dyne/cm)

Figure 3 illustrates the correlation between contact angle and surface energy to the bond strength measurements between the different thermoplastic polymers and steel. Higher surface at the polymer reveals superior bond strength with steel, as measured by lap shear strength test. The value of surface energy has direct relationship with the amount of polar groups or reactive ions at the surface of the polymer; thus PP, which lacks of free radicals in its polymeric chain has the lowest surface energy. Soft TPU with –NH and –C=O functional groups and PP-MA with C=C,-C=O functional groups have similar surface energy close to 38 dyne/cm, which allows the polymer to attach to steel. A surface energy above 36 dyne/cm in polymers is an indication of good adhesion with fibers of different materials (i.e. carbon, glass, Kevlar).

**Steel Coated and Uncoated:** Usually, metals have high surface energy; however to increase wettability, surface treatment was employed to impart reactive site for bonding with polymeric materials. Figure 4 shows the contact angle for steel coated and uncoated. Comparing the contact angle of the uncoated steel to Si coated steel and a C:H coated steel, Si coating provides a surface to steel with lower value for a contact angle of 79º, however the difference between the
three cases is almost insignificant (82º, 79º, 80º respectively), increasing the surface energy only by 6% as shown in Figure 4.

![Figure 4. Contact angle and surface energy for plasma treated and non-treated steel](image)

**Lap Shear Strength**: Bond strength of polymer-metal adhesion was determined by single lap shear test. Figure 5 compares the bond strength of steel to different thermoplastic polymers. PP-MA and TPU bond with similar strength to steel, which confirms the previous analysis of molecular characterization and wettability of these polymers. PP-MA exhibits bond strength of 3.18 MPa vs 3.25 MPa for soft TPU. PP-MA has close to the double the value on bond strength compared to neat PP (3.18 vs. 1.47 MPa).

PAPCVD was used to add specific molecules on the metal surface that can diffuse into the bulk polymer and create a stronger interface. This interface represents the elimination of distinct joining surfaces, and replaces it with a relatively smooth gradient from the metal to the polymer. Molecules of silicon, hydrogen and carbon interact with the surface of PP-MA. The surface of PP-MA offers active radicals of -C=O that interact with the molecules on the steel surface after the plasma treatment. Figure 4 showed the effect of plasma treatment on steel on the bond

![Figure 5. Effect of polymer type on the bond strength at the polymer-steel interface.](image)
strength of PP-MA. The bond strength is not only a function of the roughness of the steel surface but also of the type of coating on the steel. Silicon coating promotes better adhesion, however hydrogenated coated (a-C:H-steel) decrease the bond strength with PP-MA.

SUMMARY

Functionalization of polymers has been analyzed in this work. PP one of the most used polymers due to its low cost, good mechanical properties and easy processing can be modified with maleic anhydride to add polar functional groups and improve adhesion with steel. Thermoplastic polyurethane is also a good option to generate adhesion with metal surfaces due to the high content of polar groups that increases wettability of the polymer, even though the mechanical properties are lower. Adversely, epoxy with fullerenes failed in the purpose of increasing adhesion mainly due to the presence of surface voids during the curing process.

Silicon surface coating provides better adhesive properties between metal-to-polymer surfaces. Specifically, this technique appears to be an effective and efficient method to promote better adhesion between steel and PPMA. However, experiments showed no correlation between surface energy and bond strength for this type of surface treatment; in fact, for coated steel, wetting tension on the steel surface is not an indication of potentially better adhesion and it is possible that diffusivity is the mechanism of adhesion between coated steel and PPMA.

A correlation between contact angle in the type of polymer and bond strength was found to be directly proportional, which indicates that polar groups on the polymer surface dominate the adhesion with steel and can be predicted by the value of contact angle. Also, for the polymers in the study, the effect of wettability dominates the ability to adhere on steel.

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REFERENCES