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Correlating Surface Energies to Adhesion Data for Thermoplastic Polyolefins via Inverse Gas Chromatography

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Polyolefins are used over a wide range of industries due to their low cost and adaptable mechanical properties. However, their low surface energy makes fabricating composites and applying coatings challenging. Therefore, various surface treatments have been utilized to enhance their adhesion properties. In this paper, the surface energies of various thermoplastic polyolefins (TPO) have been measured via Inverse Gas Chromatography (IGC SEA). These surface energy values were correlated to mechanical adhesion testing of the painted polyolefins. The adhesive integrity of the painted TPO was determined by applying a comprehensive-shear load to the material. Higher surface energies measured by IGC SEA lead to increased adhesion with the paint. The surface energies also correlate with TPO crystallinity, as determined by microhardness testing of the unpainted TPO.

Introduction

Polyolefins are the most widely used commercial polymers. These materials, such as polyethylene and polypropylene, are used extensively, due to their low cost, versatile mechanical properties, low density, and excellent solvent resistance. These materials are found in applications as diverse as food packaging, garbage bags, beverage containers, and ultra-high strength fibres. Thermoplastic polyolefins (TPO) are a family of polyolefin blends consisting of impact modified polypropylene and other polyolefins (i.e. ethylene-propylene rubber and ethylene-butene rubber) as the dispersed phase. These types of materials are widely used for the fabrication of automobile parts.

Despite their wide range of applications and relative low cost, challenges exist when using polyolefins for painted or composite applications. Polyolefins typically have low surface energies, thus poor wetting characteristics. There have been several attempts to improve the adhesion by a variety of chemical treatments. Most of these techniques attempt to introduce polar functional groups to the polyolefin surface to increase the surface free energy and adhesion properties. For instance, polyolefin parts are often coated with an adhesion promoter consisting of maleated, chlorinated polyolefin or CPO [1]. Other 'adhesion promoting' methods include flame treatment and corona discharge [2] and UV irradiation [3]. Mechanical treatments have been used as well, but they are typically too aggressive and their effects are minimal [4]. In all, the goal of the above treatments is to strengthen the interfacial region between the polyolefin and paint or composite material. The integrity of the coating or composite will be determined by the ability to transfer stress to the polyolefin substrate. The strength of the interfacial bond is determined by the surface energy of the materials.

In this study surface energies of six TPO materials have been determined by Inverse Gas

Chromatography (IGC SEA). The surface energy is taken as a measure of the adhesive characteristics of the material. These surface energies were correlated with mechanical adhesion testing for the painted surfaces and microhardness of the base TPO as a mechanical measure of crystallinity.

Method

IGC SEA is a well-known tool for the characterization of particulates [5], fibres [6] and films [7]. IGC SEA involves the sorption of a vapour (probe molecule) with known physico-chemical properties onto an adsorbent stationary phase (polyolefin sample) with unknown physico-chemical properties. This approach inverts the conventional relationship between mobile and stationary phase found in analytical chromatography. The stronger the interaction, the more energetic the surface and the longer the retention time. For this reason a range of thermodynamic parameters can be derived from the retention behaviour. A detailed explanation of the theory is given in Reference [5].

One of the most commonly used parameters for the description of the energetic situation on the surface of a solid is the surface energy. The surface energy is defined as the energy required to form (or increase the surface by) a unit surface under reversible conditions and is the analogous to the surface tension of a liquid. In practical terms, the higher the surface energy the more reactive the surface. This parameter can be divided into a dispersive and a specific component. The dispersive surface energy can be directly calculated from the retention times of a series of injected n-alkanes [8]. The specific contribution of the surface energy is obtained indirectly via the specific free energy which can be obtained by injecting a range of polar probe molecules.

By applying an appropriate concept, the acid-base numbers can be calculated from the specific free energies. The study of acid-base properties by IGC SEA has the benefit that changes in the orientation of surface groups can be studied. Those changes are not necessarily related to variations in composition. For this reason spectroscopic methods are less appropriate for the study of these effects [9].

The most common approach for acid-base calculations used in IGC SEA is the Gutmann concept [10]. Equation 1 gives an approximation:

$$\Delta G_{SP} = K_a \cdot DN + K_b \cdot AN^* \qquad (1)$$

where the constants Ka and Kb represent the acid and base contribution of the solids surface while DN and AN* are the donor and acceptor number of the probe molecule. ΔGSP is the specific free energy of an individual polar probe interacting with the solid surface. Although this is very useful for semi-quantitative studies it suffers from the fact that the acid-base numbers obtained are dimensionless and can only be used for relative comparisons.

An alternative is the van Oss concept [11], which provides acid and base numbers in the same unit as the surface energy.

$$\Delta G_{sp} = N_A * a_m * 2 * ((g_L^{+} * g_S^{-})1/2 + (g_L^{-} * g_S^{+})^{1/2)}$$
(2)

In this equation □S+ and □S- are the electron acceptor (acid) and electron donor (base) parameters of the surface and □L+ and □L- are the electron acceptor and donor parameters of the probe molecule. Unfortunately, in its original form, this equation can only be used for relative comparison due to inaccurate starting parameters leading to an overestimation of the basicity [8]. Despite this, however, it is a useful concept for the determination of the specific surface energy. The specific surface energy can be obtained from the g_L^+ and g_L^- numbers according to Equation 3:

$$g_S^{SP} = 2 \times \sqrt{g_S^{+} \times g_S^{-}} \qquad (3).$$

Materials

The polymers used in this study were six thermoplastic olefins (compounded blends of poly(propylene) homopolymer, Escorene 1042 available from ExxonMobil) with different types and amounts of elastomer loading. Elastomers consisted of Exxact 3125, 4033, and 4049, all available from ExxonMobil, with a density of 0.9124, 0.8837, and 0.873 respectively. Generally, the higher the density in an elastomer the greater the crystallinity. Elastomer loadings in the TPO compounds were 12 and 25 wt %. As tested, the samples were small (< 4mm) pellets.

A commercially available adhesion promoter (AP), basecoat (BC), clearcoat (CC) system was spray applied wet-on-wet-on-wet with a 10 minute flash between AP and BC, and 6 minute flash between BC and CC. The AP consisted of a solventborne chlorinated poly(olefin) (PPG MPP6000, 0.3-0.4 mils), a one-component acrylic polyester melamine white pigmented BC (CBCF6640, 1.4-1.6 mils), and a one-component acrylic melamine CC (CUCC1000XA, 1.0-1.2 mils). The system was baked for 30 minutes at 121 oC in a gas fired oven.

IGC SEA Experiments

For an IGC SEA experiment the samples were packed into silanised glass columns (30 cm long, 4 mm ID). Prior to measurement the sample was pre-treated at 303 K for 2 hours in situ.

IGC SEA measurements were carried out using the SMS-IGC SEA 2000 system (Surface Measurement Systems, UK). The samples were measured at 303 K with a carrier gas flow rate of 10 ml/min. Probe molecules were undecane, decane, nonane, octane, dichloromethane, acetone, ethyl acetate, ethanol and acetonitrile. All solvents were supplied by Aldrich and were HPLC grade. The probe molecules were injected from the head-space via a loop with 250 µl volume. The injection concentration was 0.95 p/p_0. The deadtime was determined by a methane injection. The experiments were run four times for each sample.

Practical Adhesion

The TPO materials were painted with topcoat and the practical adhesion was determined by applying a comprehensive-shear load to the painted substrate. Compressive-shear loading was performed using a SLIDO apparatus, for which a description can be found in Reference [12]. For this test, the sample is placed on a translating stage onto which a 10.2 aluminium bob, covered with Kapton poly(imide) film, applies the loading force. The sample is then translated under the bob at a fixed acceleration of 20 in/sec2 and velocity of 2 in/sec to produce load/displacement output. The tests were performed in triplicate at testing temperatures of 68 °C. The traction force, also called the frictional force, was measured by taking the peak load in compression.

Results

The dispersive contribution of the surface energy is shown for each TPO sample in Figure 1.

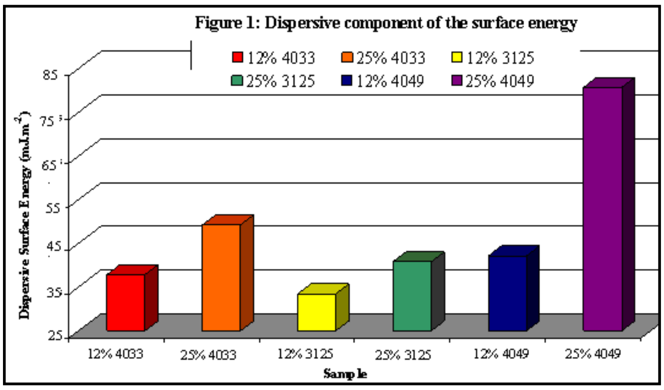

Figure 1. Dispersive surface energies of the different TPO samples measured at 303 K.

For each TPO-elastomer system studied (3125, 4033, and 4049) the dispersive surface energy increases as the elastomer content is increased from 12 wt % to 25 wt %. This is most obvious for the 4049 samples (blue and purple). Increased elastomer loading clearly makes a more active surface. There is also a general trend observed for the elastomer systems used. For the both the 12 wt % and 25 wt % samples the dispersive surface energies obey the following trend: 3125 < 4033 < 4049.

The five polar probes studied had minimal interaction with the six samples. The peaks of the five polar probes were not sufficiently separated from the methane peak, thus making determination of the free energies unreliable. Polyolefins are strictly composed of sp3 bonded hydrocarbons, which would be dominated by dispersive interactions. Therefore, it is not surprising that the TPO surfaces had minimal interactions with the polar probes used in this study. Since the free energies were not attainable, the specific surface energies were not calculated. Thus, only the dispersive surface energies were used to characterize the energetic situation on the surface of the six samples.

Figure 2 shows a correlation between the dispersive surface energies obtained for the different polymers (related to thermodynamic adhesion) and traction force in kilograms required to achieve shear delamination (measure of practical adhesion).

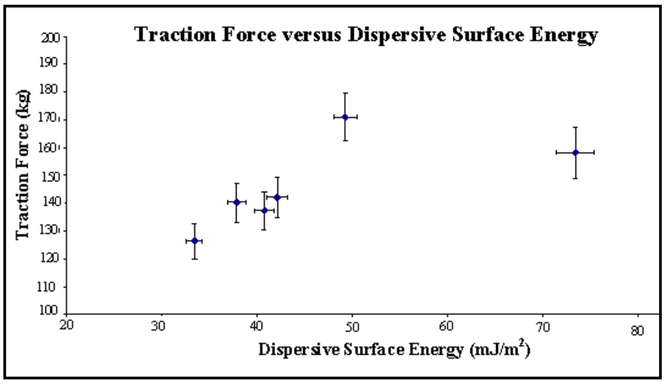

Figure 2. Correlation between dispersive surface energies (thermodynamic adhesion) and traction force required for shear delamination (practical adhesion).

The error bars in Figure 2 represent the standard deviations for the dispersive surface energies (n=4) and SLIDO performance (n=3). As Figure 2 clearly indicates, there is a strong relationship between the dispersive surface energies and traction force. As the dispersive surface energy increases, so does the practical adhesion. Therefore, this data suggests, IGC SEA could be used as a predictive tool for ultimate paint-TPO substrate performance.

The microhardness of the samples can be related to the crystallinity of the samples. The more crystalline the sample, the higher the hardness. Figure 3 displays the microhardness of the six samples versus the dispersive surface energy. Again, the error bars represent the standard deviations for the measurements (microhardness, n=3; dispersive surface energy, n=4). As Figure 3 indicates, the crystallinity increases as the dispersive surface energy decreases. Therefore, the lower the crystallinity (higher amorphous content), the higher the dispersive surface energy and higher the adhesion to paint (as determined by SLIDO performance). As the crystallinity increases the penetration of the paint will decrease correspondingly. As supported by the traction force and surface energy data, this leads to decreased paint adhesion.

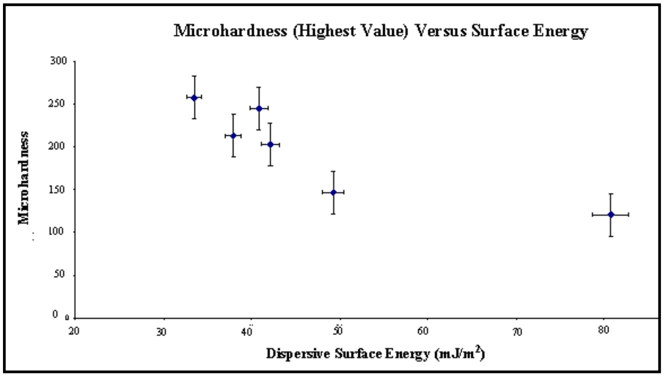

Figure 3. Microhardness (measure of crystallinity) of the six TPO samples plotted versus dispersive surface energy (as measured by IGC SEA).

Conclusion

Six TPO samples, three elastomer agents with two loadings, have been investigated by IGC SEA. For each elastomer increasing the loading increased the dispersive surface energy. Increasing elastomer loading clearly makes a more reactive surface. For both loadings, the dispersive surface energies obeyed the following trend: 3125 < 4033 < 4049.

Traction force of the painted TPO materials show a direct correlation to the dispersive surface energies measured by IGC SEA. Also, the dispersive surface energy values increased as crystallinity decreased (or amorphous content increased) as confirmed by microhardness testing. Therefore, IGC SEA could be used as a predictive tool for TPO-paint adhesion and mechanical substrate performance.

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