



Polyethylene/polyurethane blends for improved paint adhesion

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ABSTRACT

Polyolefins have low free surface energy that prevents good wettability of adhesives or paint emulsions to their surface. This work shows that adhesion of olefin block copolymers (OBC) to a polyurethane-based paint can be significantly improved by blending thermoplastic polyurethane (TPU) into OBC. Furthermore, blend morphologies near the paint/polymer interface, and surface compositions of injection molded plaques, were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) in order to explore the underlying mechanism of paint adhesion to TPU/OBC blends. It was found that for 35 wt% and 25 wt% TPU loading, the top paint layer is well-attached at the interface, whereas for 15 wt% loading, there was incomplete wetting of the paint, and a gap between the polymer substrate and paint was apparent. XPS and SEM gave consistent results demonstrating that outermost surface composition of TPU in these blends is slightly higher than in the bulk. It is speculated here that, during painting and the subsequent drying step, polyurethane chains from the paint diffuse into the blend substrate and entangle with TPU in the blend. The entanglement between paint and substrate generates a physical link that provides adhesion.

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1. Introduction

Polyolefins (PO) are the largest family of commercial polymers. The main commercial drivers for this success are their excellent cost position, mechanical properties, environmental and energy footprint, recyclability, and chemical resistance [1,2]. Some of the applications where PO are used demand that the part is painted. These include automotive and consumer goods. However, the intrinsic non-polar surfaces of polyolefins inevitably lead to poor paint adhesion.

To achieve the adhesion between a polyolefin substrate and a paint, various surface modification technologies have been developed, such as flame or plasma treatment [3], or application of chlorinated and non-chlorinated adhesion promoters [4]. Although these surface treatments can lead to enhanced paint adhesion, there are shortcomings associated with each of them. Chlorinated and non-chlorinated chemicals and organic solvents are not desirable from an environmental point of view, and flame or plasma treatment require extra investment in infrastructure and manufacturing time.

Over the past decades, blends of PO with polar polymers have received attention as an easy route to enhance the adhesion of

polyolefins [5]. It has been shown that near-surface morphology of the unpainted and painted injection molded polyolefin plaques is of primary importance in controlling the paint adhesion to the polyolefins [6]. Characterization techniques, such as X-ray microfocus fluoroscopy [7], visible-light differential interference microscopy [8,9], and photo-acoustic Fourier transform infrared spectroscopy [10], have been used to determine the polyolefin surface morphology. These are indirect observational techniques and the practical spatial resolution limits of all of these techniques are on the order of several micrometers. Direct observational techniques and better resolutions are needed.

In this study, in order to enhance the adhesion between a polyurethane paint and an olefin block copolymer (OBC), thermoplastic polyurethane (TPU) was blended into OBC. This study is aimed at determining the mechanism of paint adhesion associated with these blends, specifically the blend morphology near the paint polymer interface and the TPU composition on the surface.

2. Experimental

2.1. Materials

OBC and TPU were provided by The Dow Chemical Company. INFUSETM 9500 is a polyolefin elastomer (POE) with blocks of hard (highly rigid) and soft (highly elastomeric) segments. The

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melting point of this polymer is 119 °C and crystallinity 18%. This polymer has a density of 0.877 g/cm³, melt index of 5.0 g/10 min (190 °C/2.16 kg) and zero shear viscosity of 1.4×10^3 Pa·s at 200 °C.

The TPU we used is a polytetramethylene glycol ether-based polyurethane elastomer with 25 wt% hard segment composed of 4,4'-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol. The molecular weight of the polyol is 2000 g/mol. The zero shear viscosity of this TPU is 1.2×10^3 Pa·s at 200 °C. The paint used is a 1 K polyester diol-based polyurethane paint (Marbo, Italy) with ethyl acetate and butyl acetate as the major solvents.

2.2. Blend preparation

Three compositions were prepared: 15, 25 and 35 wt% of TPU. These samples were prepared either by compounding with a twin screw extruder (TSE) or by dry blending. The former are C₁, C₂ and C₃, and the latter P₁, P₂ and P₃.

C₁, C₂ and C₃ were prepared on a Werner and Pfleiderer ZSK-25 compounding extruder. The TPU and OBC pellets were fed through separate weight loss feeders that were controlled to feed in the ratio of the desired composition. Between 2 and 5 wt% of maleated polyethylene based elastomer was used to aid dispersion of the TPU in the OBC. This elastomer was dry blended with the polyolefin component and fed together with the polyolefin. A temperature profile of 140 °C in zone 1 and 170 °C in zone 2 through zone 8 was used. The extruded strand was pelletized and dried overnight in a conventional static oven at approximately 80 °C to remove residual moisture.

The dry blends, P₁, P₂ and P₃ were dry blended from pellets and fed directly into the injection molder. The same formulation ingredients described above were used in this dry blending study.

2.3. Injection-molded plaques

Injection molding was carried out on an Arburg 370C, 80 ton injection molder using a plaque mold with dimensions 10.2 cm × 15.2 cm × 0.32 cm. No mold release was applied. The nozzle temperature was set at 200 °C. Mold temperature was 18 °C. The injection molded plaques were held at 600 bar for 30 s.

2.4. Paint adhesion test

Fig. 1 shows the procedure used to evaluate paint adhesion based on ASTM D3359 method B and DIN Standard 53151. Samples are cleaned once with a wipe (Kimberly-Clark KIMTECH Science) soaked with toluene and allowed to fully evaporate afterwards. Painting is applied with wire rods that lay down a dry thickness of 15–20 μm. Plaques are dried at room temperature for four days. The surface of each painted plaque is scratched with a tool holding 11 cutting blades, separated from each other at 2 mm distance, both vertically and horizontally, thus creating 100 small squares of 4 mm². A strip of adhesive tape (TESA™ Tesafix 04970-00154-00) is applied with constant pressure which is released after 1 min. The

tape then is pulled at 90° to the plaque surface. The experiment is repeated a second time with a new piece of tape. The percentage of squares where the paint is still intact is reported.

2.5. Characterization techniques and sample preparation

2.5.1. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a Surface Science SSX-100 spectrometer using a focused monochromatic Al Kα anode ($h\nu = 1486.6$ eV) and a spot size of 800 μm. Electrostatic charging was neutralized by mounting a nickel grid about 2 mm above the sample surfaces. Accelerating voltage of 10 kV was used for data acquisition. After reflections corresponding to binding energies of C_{1s}, O_{1s} and N_{1s} were identified, higher resolution spectra were recorded for elemental quantification. The recorded spectra were adjusted to the C_{1s} peak of the saturated hydrocarbon bonds at a binding energy 284.6 eV. Samples were cut near the center of injection molded plaques and cleaned once with a wipe soaked with toluene. Then the toluene was allowed to fully evaporate. The elemental compositions were quantified from the peak areas using Wagner's sensitivity factors [11] and the spectrometer transmission function was taken into account. The parameters used for fitting were the peak area, the peak full width at half maximum, the position of the peak maximum, and the Gaussian–Lorentzian ratio.

2.5.2. Scanning electron microscopy (SEM)

SEM images were taken with a JEOL 6500 scanning electron microscope with a field-emission gun. Samples were cut from near the center of the painted injection molded plaques and then cryo-microtomed in the direction parallel to the interface. All SEM samples were stained in RuO₄ vapor for 20 min. Cracks were generated at the interface to observe the microstructure during delamination. Electron beam current and potential were varied for optimal imaging. Small working distance of ~4 mm was used to observe surface detail. Thresholding image analysis was applied for surface composition calculation.

2.5.3. Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR)

A Fourier-transform infrared spectroscopy (FTIR) (Nicolet Series II Magna-750, Thermo Fisher Scientific Inc., Waltham, MA) equipped with a single bounce attenuated total reflectance (ATR) attachment (Profilir TM, SpectraTech, Oak Ridge, TN) and a mercury–cadmium–telluride detector was used to collect spectra. Samples were cut using a razor blade from the center of unpainted injection molded plaques and a total of three samples were tested for each plaque. The sample was pressed against the ATR crystal to ensure complete contact. A total of 512 scans were taken on each sample over the wavelength range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

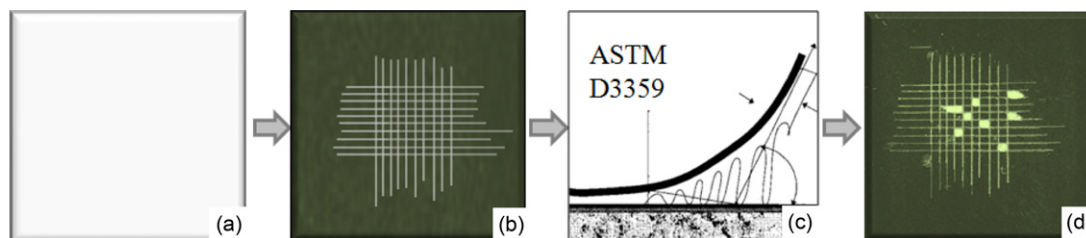


Fig. 1. Procedures for testing paint adhesion based on ASTM D3359 method B and DIN Standard 53151. (a) Prepare plaques via injection molding, (b) spread PU paint with wire rods. Cut the paint layer into 100 small squares after paint is fully dried, (c) apply adhesive tape and peel and (d) report the percentage of squares with intact paint.

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