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Measuring Adhesion to Poly(olefins): The Role of Adhesion Promoter and Substrate

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The use of thermoplastic poly(olefins) in the automotive industry continues to proliferate due to their decreased cost and weight and increased recyclability in comparison to thermoplastics such as poly(carbonate) alloys or poly(urethanes). An attribute that continues to hamper the widespread introduction of thermoplastic poly(olefins), in particular thermoplastic olefin (TPO, a blend of impact copolymer and elastomer), into additional automotive components, however, is its poor surface wettability and adhesion. Adhesion promoter formulation, both in terms of resin composition and solvent variation, has been known to influence the adhesive propensity of topcoats when analyzed by typical tests such as peel strength. It has long been disputed, however, that peel strength is not a true measure of paint adhesion since it artificially introduces a film between the paint and the adhesion promoter to enable one to perform the test. In contrast, this paper discusses the use of a newly developed in-situ adhesion test, described as compressive shear delamination (CSD), to quantify the adhesive/cohesive propensity of coatings to a variety of TPO substrates. The effect of solvent type and chlorinated poly(olefin) (CPO) adhesion promoting resin on the adhesion/cohesion of topcoats to TPO is described. Chlorinated poly(olefin) type, followed by solvent variation, was shown to have the most significant impact on the adhesion/cohesion of topcoats. This newly described CSD protocol for determining the weak link in painted plastic may have a significant impact on the choice of topcoat, adhesion promoting primer formulation, and substrate in particular automotive applications.

INTRODUCTION

Global plastic consumption in automotive applications last year was estimated to be 6,917 metric tons, with a growth rate of 5 to 10% (dependent upon plastic type, e.g., commodity, engineering, etc.) expected through the year 2020.[1] Thermoplastic olefins account for roughly 75% of the materials utilized in exterior applications (fascias, rocker panel moldings, etc.) while they account for nearly 30% of interior plastics. These percentages are expected to grow to roughly 85% and 60%, respectively, by the year 2007. It is no surprise that thermoplastic olefin (TPO), while gaining use in automotive applications due to its light weight, low cost, and recyclability, still remains somewhat of a nuisance for painters due to its inherently low surface free energy which often times results in poor wettability and low adhesive strength.

Compounding the problem is the shear sensitivity of TPO in its fabrication. Fabrication methods such as injection molding are most commonly utilized in forming automotive parts. The injection molding process, however, retains a high cost of capital due to the equipment and tooling utilized. Therefore engineers would like to produce as many parts per hour on this equipment to attain payback in shorter periods of time. The high shear rates accomplished within the semi-crystalline TPO plastic, due to high filling velocities of the molten pellets into the tool, imparts the shear dependent morphology experienced in injection molded fabricated TPO parts.[2-4] The shear induced morphology resultant from the injection molding process imparts boundary layering, the thickness and intercompatibility of which determines the ultimate cohesive tensile strength of the plastic alloy.[5]

Adhesion to an untreated (e.g., no flame- or plasma-pretreatment) weak boundary layered TPO plastic is dependant upon the ability of an adhesion promoting primer formulation to wet out the surface, diffuse into the top subsurface morphology, and swelling and entanglement

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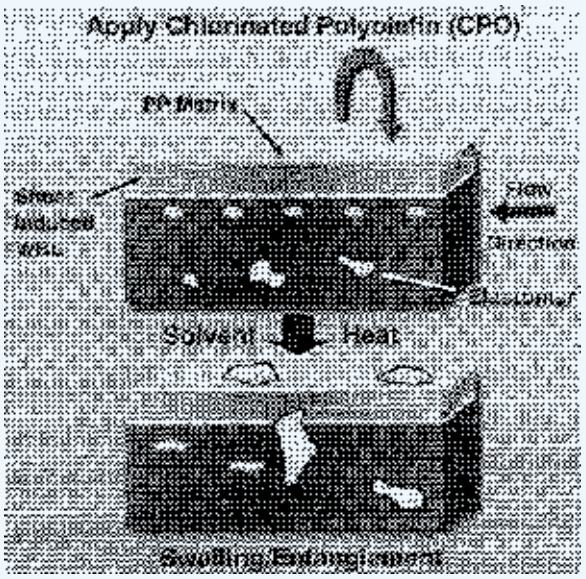

Figure 1—CPO diffusion, swelling, entanglement, and resultant adhesion within TPO.

of the adhesion promoting resin with the amorphous regions (e.g., elastomer or amorphous poly(propylene)) of the plastic substrate[6-9] (*Figure* 1).

The type of chlorinated poly(olefin) (CPO) utilized in enhancing adhesion to the TPO substrate was found to be influenced not only by the crystallinity of the CPO, which is influenced in part by the degree of chlorination, but also by the degree of maleation on the CPO backbone.[10,11] Higher maleation levels were found to provide greater topcoat interlayer adhesion with the CPO containing adhesion promoter, while CPO formulations with higher chlorine levels resulted in poorer gasoline resistance of the topcoated composite (higher chlorine levels resulted in greater solvency of the adhesion promoter in gasoline, thus resolvation). Solvent levels in the adhesion promoting primer formulation were also found to influence resultant topcoat adhesion, as evidenced through cohesive integrity in thermal shock resistance testing.[12]

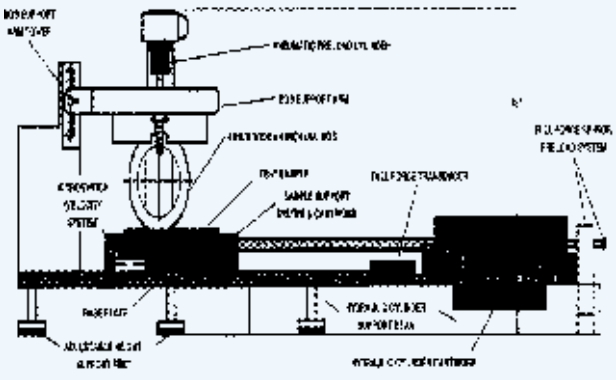

Figure 2—SLIDO compressive shear delamination apparatus.

The effect of topcoat type, however, on the resultant adhesive/cohesive integrity of painted TPO composite was evaluated through the use of a device capable of applying a compressive-shear load to the part.[13] A schematic of the device, herein termed SLIDO, is shown in *Figure* 2. In the SLIDO compressive shear delamination (CSD) testing protocol, the sample to be tested (e.g., a painted TPO plaque) is placed on a translating stage (referred to as the "test panel" area in the figure) onto which a 10.2 cm (4 in.) aluminum bob applies the loading force. The panel, heated if desired by infrared heaters located above and on top of the panel area, is then translated under the bob at a fixed acceleration and velocity to produce an instrumented load/displacement profile output.

When damage is incurred within a painted TPO part, e.g., the fascia, the customer does not discern whether the damage is adhesive or cohesive (*Figure* 3). As depicted in *Figure* 3, the damage incurred within the painted TPO substrate is most often cohesive in nature (as evidenced by the dark gray TPO ripping cohesively under the white basecoat/clearcoat painted substrate). The corrective action taken by the automotive supplier to alleviate such damage should be one in which the painted substrate is made more robust cohesively. Early studies indicated, however, that by simply changing the topcoat type the early damage resistance of the painted TPO could be made more robust.[13] Painted TPO damage, however, was not alleviated completely. It was still noted that field returns were cohesive in nature, and that fixes imparted to the clearcoat, namely decreasing the coefficient of friction by increasing slip-aid concentration, were only temporary due to the loss of slip-aid over time in the field.

Upon exposure to compressive shear events (e.g., a fascia running into a pole, a shopping cart bumping into the rear bumper of a car) failure within the painted substrate is most often the result of cohesive ripping within the TPO weak boundary layers. Removal of topcoat and fibrillation of the elastomer or amorphous poly (propylene) from the top plastic surface evidence the failure. In addition to topcoat coefficient of friction contributing to initial damage resistance, topcoat surface hardness and topcoat tensile strength, as determined through essential work calculations, were also found to contribute to the ability of the painted part to resist damage.[13]

Little conclusive all-encompassing work has been done to study the effect of an adhesion promoter or topcoat type on the resultant adhesion/cohesion of paints to TPO. Early work in fracture mechanics studies[14,15] did show that by varying topcoats different "adhesive" levels to the substrate were afforded, but little was done to study the mode of delamination, with comments such as "failure within the topcoat" or "failure to the substrate" made. Formulation variables in topcoats, in particular adhesion promoters, and their effect on adhesion/cohesion of paint systems to TPO are published modestly, at best.

Peel strength measurements have recently been undertaken in the coatings for plastic arena in attempts to define adhesion promoter capabilities.[16,17] In the peel strength method, however, it is difficult to discern the actual mode of failure due to the intrusive nature of the "fabric" uti-

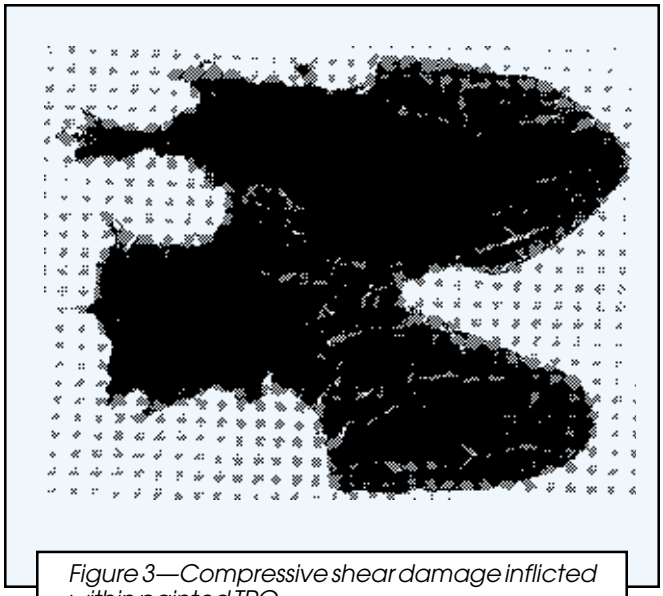

Figure 3—Compressive shear damage inflicted within painted TPO.

lized in the test to enable peel within the paint. The fabric utilized in the test is most often placed between the basecoat and clearcoat layers of the painted substrate. In the peel test, peel is accomplished at either 90° or 180° relative to the plane of the painted part. Resultant adhesive/cohesive loss is afforded in terms of kg/cm of failure.

Adhesive testing methodology thus far described and accomplished does little to help the coating formulator improve either the adhesive or cohesive strength of the painted plastic independently. We undertook this work for two reasons: to improve the test methodology utilized in evaluation of the adhesive/cohesive propensity of coatings to plastics, in particular to develop a reproducible test that relates to real world use profiles; and to study the effects of formulation variations, e.g., solvent changes, adhesion promoter changes, and topcoat variations, on the resultant adhesive/cohesive robustness of painted TPOs.

This paper discusses the use of a newly developed in-situ adhesion test, described as compressive shear delamination (CSD), to quantify the adhesive/cohesive propensity of coatings to a variety of TPO substrates. The effect of solvent type and chlorinated poly(olefin) (CPO) adhesion promoting resin on the adhesion/cohesion of topcoats to TPO is described. Chlorinated poly(olefin) type, followed by solvent variation, was shown to have the most significant impact on the adhesion/cohesion of topcoats. This newly described CSD protocol for determining the "weak" link in painted plastic may have a significant impact on the choice of topcoat, adhesion promoting primer formulation, and substrate in particular automotive applications.

EXPERIMENTAL

Substrates were obtained from Custom Precision Molding, Romulus, MI, as 10.2 × 30.6 × 0.3 cm (width × length × thickness, respectively) top-gated injection molded precolored (dark gray) plaques. All coating formulations utilized in this study were provided by Red Spot Paint and Varnish, Inc. Coatings were spray applied with conventional air atomized guns to the substrate specified and baked for 30 min ambient at 121°C in a gas fired oven. Film thickness measurements were made by cross-sectioning the part and analysis of the cross-section with an optical microscope. All film thicknesses were in the following ranges: adhesion promoter, 7.5 µm; white basecoat, 43 µm; and clearcoat, 50 µm. All multiple layer (e.g., adhesion promoter/basecoat/clearcoat) coatings were applied wet-on-wet with a three-minute ambient temperature flash after adhesion promoter, a five-minute ambient temperature flash after basecoat, and a five-minute ambient temperature flash after clearcoat and before oven. Coatings were allowed to post-cure after final bake for 72 hr prior to testing.

Peel strength tests were performed as described in reference 16.

Fracture toughness (G_c) results were obtained through the methods described in reference 14.

SLIDO testing was performed on the apparatus described in reference 13, and shown in *Figure* 2. As shown in the figure, a painted panel is placed under the bob (an aluminum counterface with a 10.2 cm diameter) covered with a polyimide film. The bob is translated across the surface of the panel at a preset loading rate with a known velocity and acceleration. The temperature of the plaque can be maintained at above ambient temperatures through use of infrared heaters located in the apparatus. Resultant plots are obtained from load versus displacement, through which the coefficient of friction of the coating can be calculated. Values obtained from the test plot also include the compression force (kg) to failure, defined as the force exerted perpendicular to the coating, and the traction force (kg) at failure, defined as the force exerted parallel to the coating. Actual conditions utilized in the SLIDO testing were as follows: 15.3 cm run length (defined as the dis-

Table 1—SLIDO Traction Results, Peel Strengths, and Fracture Toughness Values for Selected Systems

CPO	C	E	A	B	D	F
Peel strength (kg/cm)	5.33	5.68	6.48	5.82	10.68	5.92
G_c (J/m^2)	450	650	900	650	700	650
Traction force (kg)	189.5	189.1	194.5	155.9	163.6	168.6
M_w	69400	82300	59700	45000	45000	45000
M_w/M_n	2.59	2.72	2.66	3	3	3
Cl (wt%)	24.5	20	18	21	23	22
MAH (wt%)	3	2.7	3.5	1.2	1.2	1.2
Peel rank	6	5	2	4	1	3
G_c rank	4	3	1	3	2	3
Traction rank	2	3	1	6	5	4

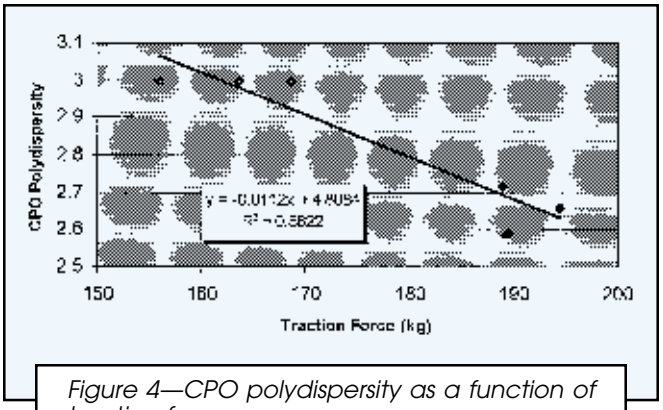

Figure 4—CPO polydispersity as a function of traction force.

tance traversed by the bob on the panel); acceleration of 50.8 cm/sec^2, velocity of 5.1 cm/sec, and a temperature of 68.3°C. Error associated with the test measurement was attained through a gage reliability and reproducibility measurement and found to be eight percent.

Plastic moduli (H_{plas}) and the degree of plastic deformation (plasticity, defined by the plastic work in the indentation unloading, W_r, divided by the total work of indentation, W_t) were measured on painted and unpainted specimens with a Fischer H100 microhardness apparatus. The apparatus was equipped with a Vicker's indentor while a load of 100 mN was applied with a loading frequency of 60 steps/1 second between steps.

Dye penetration values were obtained from cryogenically cracked cross-sections (cracked to obtain a fresh edge) of unpainted TPO substrates that had been exposed topically to 1 ml of fluorescent dye solution for 30 min at room temperature (25°C). The dye solution was made up of a solution of 0.5 wt% 7,7'-dimethyl-4-aminocoumarin dissolved in the solvent of choice (Aromatic 100, xylene, or a 1:1 wt/wt xylene/toluene; solvents utilized as received from Aldrich Chemical Co.). The TPO sections were photographed using an Olympus BH-2 fluorescence microscope with a violet excitation filter (Olympus V BP-405) in combination with a dichroic mirror V (DM-455 + YM-455) and an additional barrier filter (Y-475 and up). Photomicrographs were made with a 20X objective and 3.3X photo-ocular using high-speed color negative film, Kodak Ektapress 400 Plus. All were exposed for identical times of nine seconds. The film was processed normally. Each frame was then measured with a MacBeth process densitometer, which had been rezeroed with respect to the film base density/color cast for intensity as well as blue. Each frame was measured in four different areas; the readings were then averaged to arrive at the data points indicated in *Table* 4. Because the readings taken are of negative film, the optical density in the photograph actually represents the color of the fluorescence, e.g., the greater the blue optical density, the bluer the fluorescence.

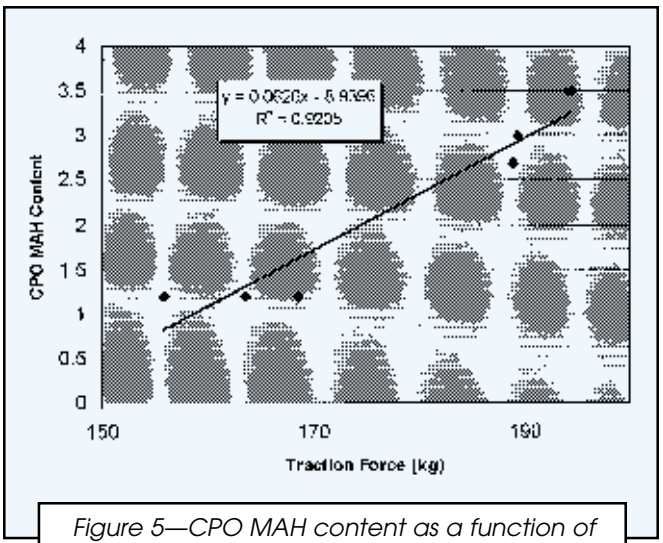

Figure 5—CPO MAH content as a function of traction force.

Essential work values were obtained by the methods described by Gregorovich and McGonigal.[18]

Dynamic mechanical thermal analysis (DMTA) was performed on a Universal V2.4F TA instruments dynamic mechanical thermal analyzer. Clearcoat films (11 × 6.4 × 0.3 mm) were placed in a film tension clamp and glass transition values (T_g, taken as the maximum of the tan delta peak) were obtained at a fixed frequency of 11 Hz, an amplitude of 0.2 mm, and a temperature ramp of –20°C to 80°C run at a ramp rate of 2°C per minute.

Optical analysis of 30 µm thick unpainted or painted specimens, obtained by cryogenically microtoming the specimens (direction of cut was parallel to the flow direction in the plaque) using Histoprep media, utilizing a Leica microscope equipped with cross-polarizing filters, afforded boundary layer thicknesses. The samples were mounted in Canada balsam between two microscope slides prior to analysis. Depths of boundary layers within the specimens were measured utilizing Optimus optical imaging software.

RESULTS AND DISCUSSION

Varying performance measures of adhesion/cohesion (peel strength and fracture toughness, as well as SLIDO traction forces) of a topcoat system with varying adhesion promoter types on a reactor grade TPO substrate (AMTUF™ 3110, BP Amoco Polymers) were determined. Painting was accomplished with a one-component (1K) basecoat/two-component (2K) clearcoat topcoat system (Red Spot 379S with slip-aids) over a series of varying CPO adhesion promoters. The results displayed in *Table* 1 are the average of three readings taken for each test. Selected properties of the CPO resins utilized, to include: weight average molecular weight (M_w); polydispersity index (M_w/number average molecular weight , M_n); chlorine content (Cl); and maleic anhydride content (MAH), are also given in *Table* 1.

The adhesion promoters were formulated with CPO resin and solvent only, neither pigment nor co-resin was added. The test rankings, from best (rated 1) to worst (rated 5 or 6), of each painted substrate for each test are also listed, the results of which will be utilized for Spearman rank correlation discussed later in this section. Other direct correlation between the responses tested will be discussed as well.

Table 2—SLIDO Traction Force Results for Selected Systems

Solvent	CPO	Substrate	Clearcoat	Traction Force (kg)	Solvent	CPO	Substrate	Clearcoat	Traction Force (kg)
Xylene	A	1440	379S	96.8	Xylene	A	1440	317LE	95.7
AR 100	A	1440	379S	74.2	AR 100	A	1440	317LE	81.9
Xyl/Tol	A	1440	379S	83.1	Xyl/Tol	A	1440	317LE	86
Xylene	B	1440	379S	108.1	Xylene	B	1440	317LE	100
AR 100	B	1440	379S	82.3	AR 100	B	1440	317LE	96.2
Xyl/Tol	B	1440	379S	96.3	Xyl/Tol	B	1440	317LE	98.8
Xylene	D	1440	379S	104.3	Xylene	D	1440	317LE	114.4
AR 100	D	1440	379S	85.1	AR 100	D	1440	317LE	96.1
Xyl/Tol	D	1440	379S	103.3	Xyl/Tol	D	1440	317LE	100.5
Xylene	C	1440	379S	103.5	Xylene	C	1440	317LE	102.9
AR 100	C	1440	379S	88.3	AR 100	C	1440	317LE	99.9
Xyl/Tol	C	1440	379S	99.9	Xyl/Tol	C	1440	317LE	102
Xylene	A	3110	379S	88	Xylene	A	3110	317LE	98.5
AR 100	A	3110	379S	95.2	AR 100	A	3110	317LE	76.5
Xyl/Tol	A	3110	379S	88.3	Xyl/Tol	A	3110	317LE	78.6
Xylene	B	3110	379S	107.9	Xylene	B	3110	317LE	110.3
AR 100	B	3110	379S	111.3	AR 100	B	3110	317LE	96.7
Xyl/Tol	B	3110	379S	105.6	Xyl/Tol	B	3110	317LE	100
Xylene	D	3110	379S	106.5	Xylene	D	3110	317LE	144.8
AR 100	D	3110	379S	111.8	AR 100	D	3110	317LE	116.1
Xyl/Tol	D	3110	379S	105.2	Xyl/Tol	D	3110	317LE	134.3
Xylene	C	3110	379S	99.1	Xylene	C	3110	317LE	115.6
AR 100	C	3110	379S	115	AR 100	C	3110	317LE	105.6
Xyl/Tol	C	3110	379S	102	Xyl/Tol	C	3110	317LE	114.1

A Spearman's rank correlation technique was utilized to compare the results obtained from peel strength and fracture toughness testing with the SLIDO traction force test results. This method was chosen for correlation rather than strictly limiting relationships to those derived from each other because of the varying error associated with each of the methods of measurement (as determined by gage reliability and reproducibility (Gage R&R)). Because of the varying levels of noise attained in the system due to slight variations in film build, substrate molding history, flash and bake times, etc., we chose the Spearman's rank technique to afford a general relationship between the factors studied. Also, each test method has a varying degree of error associated with it, and we did not perform a gage R&R on each of them.

In the Spearman's rank correlation technique a correlation coefficient to goodness of fit is established via equation (1):

$$R = \frac{1 - 6d^2}{n^3 - n} \quad (1)$$

where: R = correlation coefficient

d = difference in relative rank between test ratings (e.g., if in the peel test the sample has a relative ranking of 3 and in the SLIDO test the same sample ranks a 1, the d value would be 2)

n = the number of samples tested (in *Table* 1 the number of samples tested is 6)

CPO Resin Attributes: Effect on Adhesion/Cohesion

The goodness of fit calculations for the peel test results and the fracture toughness test results versus the SLIDO traction force results on the same samples were 1.20 and 0.65, respectively. These results indicate that the peel test and fracture toughness test results agree within 80% (1.20 represents an overestimate from 1 by 20%, or 0.8) and 65%, respectively, with the SLIDO test results obtained. The peel strength results overestimate the adhesion/cohesion of the coatings to the TPO substrates, when compared to the traction force results, while the fracture toughness test results underestimate the adhesion/cohesion of the same coating systems when compared to traction force results. All in all, however, since the results correlate with at least a 65% goodness of fit, there is a reasonable probability that the best coating system for the reactor grade TPO evaluated in this study is that which utilizes the CPO resin with the lowest chlorine content, a high level of maleic anhydride, and a relatively low polydispersity index. These results also suggest that the SLIDO traction force results obtained via the new CSD testing methodology utilized herein may provide a reasonable means to assess the adhesive/cohesive integrity of painted TPO systems.

When the CPO polydispersity is plotted versus the SLIDO traction force a direct correlation, correlation coefficient of 0.88 to linear behavior, is apparent (*Figure* 4). The lower CPO polydispersity resins result in higher traction forces. This relationship is somewhat expected if one considers the major mode of adhesion to be due to diffusion of CPO into the TPO and resultant entanglement. Lower polydispersity resins, if they retain the same relative weight average molecular weight, should result in higher diffusion rates and greater entanglement. The polymer chains in the narrower polydispersity resin are of more consistent molecular weight and would result in more consistent entanglement, having less low molecular weight species which result in poorer entanglement, and less high molecular weight species which would result in poorer diffusion.

Table 3—Representative Attributes of Clearcoats Utilized

Clearcoat	H_{plas} (N/mm2)	T_g (°C)	W_{ess} (x 10^{-3} J)
317	205	34.03/54.85	4.55
379	285	48.60/62.45	9.55

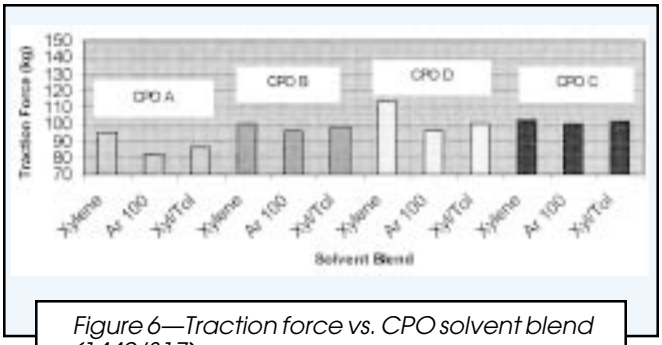

Figure 6—Traction force vs. CPO solvent blend (1440/317).

Table 4—CPO/Solvent Blend Viscosity Profiles

CPO	Solvent/Viscosity[a] (cps) Xylene	Aromatic 100	1:1 Xylene/Toluene
A	590	1140	302
B	62	110	42
D	192	350	194
C	62	84	62

(a) #3 Spindle, Brookfield viscometer, 50 rpm.

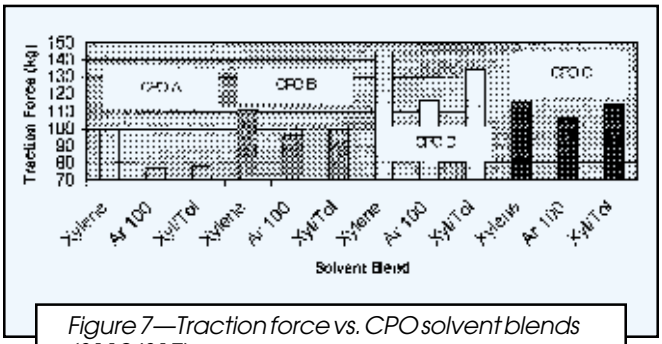

Figure 7—Traction force vs. CPO solvent blends (3110/317).

The effect of maleic anhydride (MAH) content on the CPO backbone is also shown to affect the SLIDO traction force, as demonstrated in *Figure* 5. An excellent correlation (correlation coefficient of 0.92) to a linear relationship is obtained. The effect of MAH on the CPO backbone is one of compatibility. As the CPO MAH content increases, the traction force also increases. It is conceivable that the MAH aids in cross-compatibility of the basecoat/clearcoat with the adhesion promoter, resulting in better intercoat cohesion and higher traction forces.

A few relationships were developed in the work described previously for the effects of CPO type on the resultant adhesion to reactor grade TPO. In the studies described, the solvent blends (40/40/10/10 Toluene/Xylene/Aromatic 100/Aromatic 150 wt/wt/wt/wt) and solids levels (10 wt% CPO) were kept constant but the viscosity of the resultant blends was not measured. The effect of CPO formulation viscosity should have significant impact on diffusion, with the lower viscosity solutions displaying a greater tendency to solvate and permeate into the substrate. The viscosity relationship to traction force will be discussed later in this section.

TPO Type/Topcoat Type/and Solvent Attributes: Effect on Adhesion/Cohesion

The effect of topcoat type on resultant adhesion/cohesion within painted TPO materials was also not evaluated in the studies perviously performed. From previous work[13] the topcoat type was found to influence subsequent damage resistance of painted plastic substrates. Coefficient of friction, toughness, and hardness attributes of the coating were shown to affect chip, mar, and gouge resistance.[19-21] Topcoat variations and their effect on traction force results will be discussed later.

The effect of TPO substrate, e.g., a reactor grade versus a physically compounded grade, was also not evaluated. Substrate surface morphology, effective hardness, and shear layer structure, should also play a significant role in the ability of adhesion promoters to penetrate and adhere to the TPO, either adhesively within the paint/TPO boundary, cohesively between the paint (e.g., basecoat to adhesion promoter), or cohesively within the substrate (e.g., boundary layer cohesion). Solvent selection is very important in painted TPO substrates (*Figure* 1) since the solvent must aid in CPO penetration and entanglement with the surface. At the same time, however, the solvent choice must not possess too slow an evaporation profile in TPO substrates with low weak boundary layer cohesion because in these scenarios the retained solvent will swell and potentially weaken the TPO subsurface morphology.

In attempts to determine the effects of CPO solvent formulation (solvents with low to high evaporation rates), CPO type (variances in chlorine content, polydispersity index, and MAH content), topcoat type (vary coefficient of friction, hardness, and toughness), and substrate type (reactor grade and compounded TPO) on the adhesion/cohesion of painted TPO substrates, a series of topcoats (1K basecoat/2K clearcoat containing no slip aids), CPO adhesion promoters (labeled A through D), solvents, and substrates were evaluated in the SLIDO traction force protocol (*Table* 2).

The topcoat systems evaluated utilized the same basecoat but varied in clearcoat properties. The clearcoat labeled 317 possessed lower toughness values, as calculated from essential work techniques, and lower surface hardness values, as evidenced in the microhardness values (H_{plas}, representative of surface hardness) and T_g values (obtained via DMTA) than the clearcoat labeled 379 (see *Table* 3).

CPO Resin/Solvent Attributes: Effect on Adhesion/Cohesion on Compounded TPO: In *Figure* 6, the effects of variances in CPO type and solvent type on resultant traction forces are displayed. The clearcoat utilized is a 2K ure-

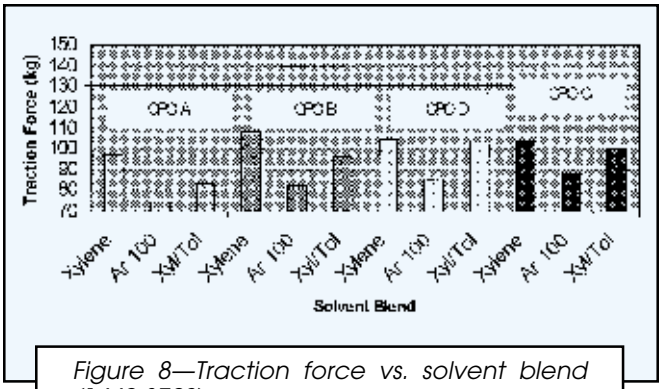

Figure 8—Traction force vs. solvent blend (1440.379S).

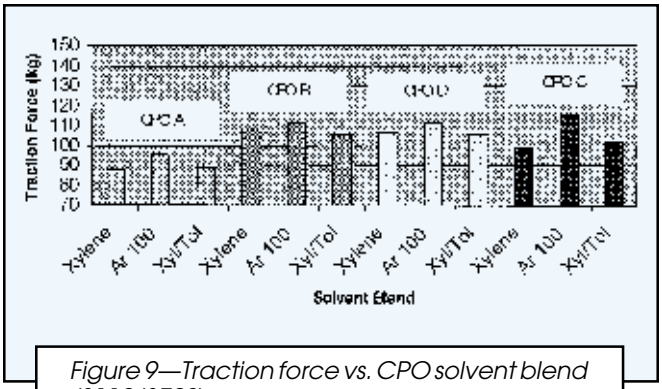

Figure 9—Traction force vs. CPO solvent blend (3110/379S).

thane with a coefficient of friction of 1.10-1.50 and an essential work value of 4.55×10^{-3} J. The substrate evaluated is a compounded grade TPO labeled 1440 (Sequel™ 1440, available from Solvay Engineered Polymers). On this substrate, with the basecoat/clearcoat described, CPO D generally affords the highest traction forces. This CPO has the opposite attributes described previously for the reactor substrate, in that it has a low MAH content, a high polydispersity index, and a high level of chlorine on the CPO backbone.

As shown in *Table* 4, however, it may be that viscosity effects of the CPO resin formulation overwhelm the CPO attributes in this case, where lower viscosity resins provide greater traction forces due more to their ability to provide greater penetration into the substrate. Solvent effects on adhesion promoter viscosity are shown in *Table* 4. All CPO formulations utilizing Aromatic 100 possess the highest viscosity, while CPO resin A affords the highest overall viscosity. The high viscosity blend (CPO A with Aromatic 100 solvent) is shown to lower the traction force, and in fact on this substrate CPO A is the worst performing adhesion promoter. This may be due to slight "kick-out" or incompatibility of the CPO resin and thus the overall results may be skewed. The low level of chlorine in CPO A would limit its solubility in solvents considered to be poor solvators. Solvent blend choice could result in lower levels of solubility, therefore future work should include a more compatible solvent blend choice.

On the compounded grade TPO substrate (Sequel™ 1440) the choice of CPO is found to influence adhesion/cohesion, as described earlier. More importantly, however, the effect of solvent seems to follow a general pattern. Even though Aromatic 100 affords the highest degree of fluorescent dye penetration (at room temperature the Aromatic 100 versus xylene/toluene versus xylene penetration depths are 93 µm, 53 µm, and 59 µm, respectively), which would potentially correlate to greater diffusion and entanglement (therefore higher adhesion levels), the Aromatic 100 CPO formulation affords the lowest traction force. This may be related to the solvent swelling effect discussed previously. The TPO substrates that possess weak boundary layers, when swollen and subjected to compressive shear loading events, lose cohesion more readily than those without weak boundary layers (or those not in the swollen state). Xylene, on the other hand, affords greater penetration depths than the xylene/toluene blend, and does result in higher traction forces. Because both of these solvent blends have relatively fast evaporation profiles when compared to Aromatic 100, they do not result in the excess post-cure swelling of the TPO substrate and thus produce results as expected, the greater penetration depths resulting in greater entanglement and adhesion/cohesion (as evidenced by higher traction forces).

CPO Resin/Solvent Attributes: Effect on Adhesion/Cohesion on Reactor TPO: As shown in *Figure* 7, when the CPO solvent blend formulations and clearcoat type are kept constant and only the substrate is changed (AMTUF™ 3110 reactor grade TPO) very similar results are obtained to those demonstrated in *Figure* 6. The coefficient of friction values do change slightly due to the effect of the substrate, from 0.7-1.2. Friction values still lie within a very similar range to those obtained with the Sequel™ 1440 described earlier so that the resulting traction force results will not be influenced by these subtle changes. Generally, higher friction values will afford greater stress within the topcoat/TPO composite and result in lower traction forces.

The CPO resins described in *Figure* 7, when formulated in xylene, afford the highest levels of adhesion/cohesion (as evidenced by the highest traction forces) while those formulated in Aromatic 100 afford the lowest. The CPO with a low MAH content, a high polydispersity index, and a high level of chlorine on the CPO backbone (CPO D) also appears to afford the highest level of adhesion/cohesion. This effect again may be more related to the lower viscosity profile of CPO resins labeled B and C and their propensity to penetrate more deeply into the TPO than to the CPO attribute relationship.

Topcoat/CPO Resin/Solvent Atrributes: Effect on Adhesion/Cohesion on Compounded TPO: To determine the effect of topcoat integrity on the resultant adhesion/cohesion within the same CPO types on the same substrates, a 2K topcoat (379S) with higher toughness (as evidenced by

Table 5—Surface Attributes of Unpainted TPO Substrates

Substrate	Hplas (N/mm²)	W_f/W_t	Birefringence (microns)
AMTUF™ 3110	60.8	0.56	59
Sequel™ 1440	75.5	0.5	29

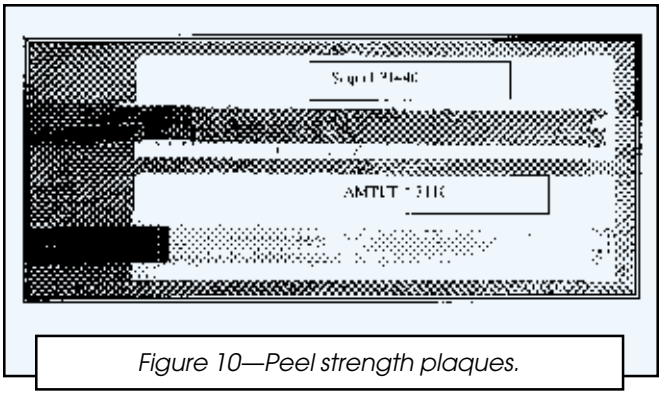

Figure 10—Peel strength plaques.

greater essential work values) and greater surface hardness than the 317 2K clearcoat utilized previously was evaluated on Sequel™ 1440 (*Figure* 8). The coefficient of friction values calculated ranged from 1.0-1.5, again very similar to those obtained with the "317" clearcoat on Sequel 1440 substrate (*Figure* 6). In these experiments similar trends to those derived in *Figure* 6 were obtained. The CPO resins formulated in xylene afforded the highest adhesion/cohesion, while those formulated in Aromatic 100 afforded the lowest. Interestingly, however, CPOs B, C, and D yielded very similar adhesion/cohesion values. It appears that a tougher clearcoat, one that is able to dissipate the applied stress within itself as opposed to through the clearcoat/basecoat/adhesion promoter/TPO interface, may tend to equalize the effect of good versus adequate adhesion promoters. The worst performing adhesion promoters, e.g., CPO A, however, still retain such a poor level of adhesion/cohesion that the clearcoat cannot compensate for the inadequacies.

Topcoat/CPO Resin/Solvent Attributes: Effect on Adhesion/Cohesion on Reactor TPO: To determine if substrate effects can overcome the influences of clearcoat or solvent effects on the adhesive/cohesive propensity described, the reactor grade substrate (AMTUF 3110) was tested under the same clearcoat as described earlier in *Figure* 8 (*Figure* 9). It is quite interesting that for the first time the adhesion promoter, when formulated in Aromatic 100 solvent, provided the greatest level of adhesion/cohesion. This would have been expected based on the high levels of diffusion of the CPO resins in Aromatic 100 versus xylene or xylene/toluene blend. It appears that for the solvent penetration depth of the CPO adhesion promoter alone to be effective, a strong clearcoat and substrate must be in place. Solvent swelling effects of the substrate, when a poor clearcoat (low toughness) is utilized, overwhelm the solvent penetration effects of the formulated adhesion promoter.

Effect of TPO Type on Adhesion/Cohesion: We have discussed a lot about traction forces in relation to clearcoat, CPO, and solvent effects on two different types of substrates. Substrate variances, e.g., reactor grade versus compounded grade, have been shown to influence the adhesive/cohesive strength of the painted TPO composite. To delineate the effect of substrate and its cohesive strength, we studied the surface morphology of the two grades of TPO previously discussed (*Table* 5). Although the Sequel 1440 appears to possess a harder surface (as evidenced by the higher H_{plas}) its viscoelastic nature (as observed from the W_r/W_t value) is more elastic than the AMTUF 3110, thereby making it more compressible. Since the Sequel 1440 is more elastic, when stress is applied to the TPO its subsurface is not as effective at dissipating the stress across the boundary layers as the stress would be in a more plastic-like substrate (e.g., AMTUF 3110). Rather, the stress is dissipated through the subsurface boundary layers, and if those boundary layers are weak they will cohesively fail (as evidenced by fibrillation or cavitation of the elastomer or amorphous poly(propylene) from the crystalline poly(propylene) phase). It is also evident from the birefringence measurements shown in *Table* 5 that the Sequel 1440 has thinner boundary layers that are more easily ripped from the substrate under compressive shear events.

If these above postulations are correct, the Sequel 1440 should fail in a different mode than the AMTUF 3110. *Figure* 10 depicts the variation in failure mode of the two substrates in the peel strength tests with the 379S clearcoat. As shown in *Figure* 10, the Sequel 1440 does experience 'fibrillation,' as evidenced by the strand-like material being pulled from the substrate upon failure. The AMTUF 3110, on the other hand, being more plastic-like does not fail in a cavitation or fibrillation mode, but rather in direct delamination of the boundary layer.

Table 6—Surface Hardness Values of Selected Systems

CPO Resin	H_{plas} (N/mm^2)	W_r/W_t
A	285	0.53
B	279	0.53
C	283	0.52
D	279	0.52

Topcoat Hardness Effect on Adhesion/Cohesion: Lastly, to be assured that variations in traction force were not due to potential retardation or enhancement of topcoat cure (and thereby resultant surface hardness values) caused by varying the CPO resins, the surface hardness values of topcoated panels were measured (*Table* 6). The systems measured were the 379S clearcoat over AMTUF 3110. As can be seen from the results, little variation is seen in either the H_{plas} or the W_r/W_t values. We thereby deduce that the CPO resin variation did not interfere with cure and thereby did not skew traction force values due to any such variation.

SUMMARY

The newly described compressive shear delamination (CSD) testing protocol has been successfully utilized to differentiate the adhesive/cohesive propensity of painted TPO substrates. The effects of chlorinated poly(olefin) adhesion promoting resins, with subsequent effects of solvent carriers utilized to apply them to the substrate, have been evaluated and ranked according to their ability to provide adhesion/cohesion of selected topcoats to the TPO.

It is important to note that the topcoat attributes, e.g., toughness, hardness, and coefficient of friction, in addition to the substrate attributes, e.g., hardness, boundary layers, and plasticity, do affect the ability of the painted TPO system to withstand applied stresses. It is not the

CPO alone, the solvent blend alone, the substrate alone, or the topcoat alone that affects the adhesion/cohesion level in the painted plastic, but rather the system attributes that do.

The effectiveness of the CSD protocol to evaluate adhesion/cohesion was evaluated in comparison to peel strength tests as well as fracture toughness tests. Correlation of approximately 65-80% to goodness of fit was achieved within the painted TPO substrates tested. The CSD testing protocol appears to underevaluate the effectiveness of the adhesion/cohesion when compared to the peel strength test, and overestimate the effectiveness of the adhesion/cohesion when compared to the fracture toughness test.

When a tough clearcoat (high toughness, hard surface, and low coefficient of friction) and a strong substrate (plastic-like viscoelasticity, deep boundary layers) is utilized, the level of chlorine level on the CPO backbone appears to have little effect on adhesion/cohesion. Rather, the chlorine level appears to play more of a role in solvating the resin in the selected solvents. Maleic anhydride content does appear to affect the adhesion/cohesion propensity of the topcoated substrate, with higher levels being more effective. Polydispersity of the CPO, assuming equivalent weight average molecular weight of the CPO, also plays a predominant role in the ability to achieve higher levels of cohesion/adhesion (with lower polydispersity performing better).

When a weak clearcoat (low toughness, soft surface, and high coefficient of friction) or a weak substrate (elastic-like viscoelasticity, shallow weak boundary layers) is utilized, the opposite trends in CPO are observed, in that higher polydispersity and lower levels of MAH are required. This trend however, may be shaded by the fact that the effective viscosity of the adhesion promoter formulation may overwhelm these results. The CPO resins with higher polydispersity and lower MAH content did afford lower viscosity than the CPO resins with lower polydispersity and higher MAH content.

Solvent type utilized to formulate the adhesion promoter resin plays a vital role in attaining adhesion/cohesion to the painted TPO substrate. The solvent appears to play three roles in providing adhesion/cohesion to the TPO substrate. For optimized performance the solvent must:

(1) Solvate the CPO resin (low viscosity of the solvated resin is desired);

(2) Provide high penetration levels of the CPO resin into the substrate (Aromatic 100 provides very deep penetration depths when compared to xylene or 1:1 xylene/toluene blends);

(3) Evaporate at a reasonable rate so that the fully cured painted substrate does not remain in a swollen-state from retained solvent.

The optimized blend of solvent should be predicated on the type of substrate and topcoat. For example, for strong TPO and strong, tough clearcoat systems, slow solvent blends should be utilized to provide maximized penetration levels of the CPO into the TPO. On weak TPO substrates or substrates painted with weak topcoats, a modified solvent blend for the CPO should be used, e.g., one that provides low viscosity of the CPO formulation and one that is not retained in the substrate after topcoat cure.

Through utilization of these testing protocol, and following the guidelines formulated from the results, paint suppliers to the automotive industry formulating for plastic parts may enhance the durability of the resultant painted plastic parts. The automotive supplier, therefore, should more aptly meet improved customer satisfaction and reduced warranty costs associated with painted plastic part implementation.

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