**IMPROVING THE ADHESION OF POLYOLEFIN ELASTOMERS**

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**Abstract**

The adhesion of polyolefin compounds to polar substrates is one of the on-going challenges for many consumer and industrial applications. Due to differences in polarity and surface energy, the bonding of polyolefin thermoplastic elastomers to engineering plastics such as PET, PA, PC, PU, and other polar materials are largely unresolved. This paper discusses the development of an adhesion primer for the surface treatment of polyolefin elastomers to improve its adhesion to PET and PC in lamination and coating processes. Results indicate that adhesion primers containing maleic anhydride functionality or a combination of MAH and chlorine functionality are effective for bonding PET and PC to a polyolefin. Overall, a combination of a surface adhesion primer and the application method can be an effective solution to provide the needed bonding. Such technology can be further applied to resolve the adhesion challenges of polyolefin elastomers to polar fabrics and coatings.

**Introduction**

The adhesion of polyolefin compounds to polar substrates is one of the on-going challenges for many applications. Due to the differences in polarity and surface energy, the bonding of polyolefin thermoplastic elastomers to engineering plastics such as PET, PA, PU, and other polar materials are largely unresolved (1). It is desirable to combine these polar substrates with polyolefin elastomers to produce composites for structural reinforcement, texturing, and abrasion resistance.

A common approach is via bulk modification, with the addition of a polar component such as a tie copolymer or a polar compatibilizer; however, as the substrate thickness increases, the bulk approach becomes less effective due to the lack of concentration at the surface. To increase the surface concentration, primer approaches are effective for targeted delivery for substrate bonding (2). Bonding examples can range from the lamination of dissimilar substrates and/or functional coatings. In these cases, a combination of a surface primer and the application method can be an effective solution to provide the needed bonding.

This paper discusses the development of surface treatment solutions based on functionalized polyolefins to improve the adhesion of a PET fabric and a PC coating to thermoplastic elastomer compounds; compounds based on ENGAGETM Polyolefin Elastomers, VERSIFYTM Polyolefin Elastomers, and INFUSE™ Olefin Block Copolymers in lamination and coating processes. Results indicate that blends with mono-functional maleic anhydride (MAH) modified (3) or bi-functional with MAH, and chlorine can be effective (4-6).

**Materials and Methods**

**Materials**

Polyolefin Sheet Preparation - Sheets of each material were compression molded in a cavity mold and press heated for 3 min at 180°C; 3mm thickness.

ENGAGETM 8200 Polyolefin Elastomer (0.87 g/cc, 5MI) (available from The Dow Chemical Company)

80/20 wt/wt blend of VERSIFY™ 3401 Polyolefin Elastomer (0.863 g/cc, 8 MFR) and INFUSE™ 9107 (0.867 g/cc, 1.0 MI) Olefin Block Copolymer (available from The Dow Chemical Company)

Adhesion Primer Preparation – Primer components were dissolved at 10% concentration in a mixture of cycloaliphatic solvents using a stirred round bottom flask, heated to 80°C. Refer to Table 1.

Primer A, B, C, D contains random ethylene-octene copolymer with different levels of MAH-functionality. The nominal density of the copolymer is 0.87 g/cc.

**Table 1 – MAH-Functionalized Adhesion Primers**

<table>
<thead>
<tr>
<th>Primer</th>
<th>% Solids Concentration</th>
<th>MAH-Functionality Level (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>None</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>Low, 0.5-1</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>Med, 1-2</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>High, &gt; 2</td>
</tr>
</tbody>
</table>

Primer E has a similar polymer composition as Primer B described above. Primer F is a blended polymer containing both MAH and chlorine functionality that are commercially available. Refer to Table 2.

**Table 2 – MAH-Cl Functionalized Adhesion Primers**

<table>
<thead>
<tr>
<th>Primer</th>
<th>% Solids Concentration</th>
<th>MAH-Functionality Level (wt%)</th>
<th>Cl-Functionality Level (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>5</td>
<td>Low, &lt; 1.0</td>
<td>None</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>Med, &lt; 1-2</td>
<td>High, &gt; 20</td>
</tr>
</tbody>
</table>

**Notes**

1. The use of terms such as “PET,” “PA,” “PC,” “PU,” and “other polar materials” is consistent with the definitions provided by the Dow Chemical Company, Freeport, TX 77541, USA.
For 2K, primer reinforcement, isocyanate crosslinker Desmodur RFE - tris(pisocyanatophenyl) thiophosphate (available from BAYER) was used.

Polycarbonate waterborne dispersion, 2k polycarbonate dispersion based PERMUTEX® WF-13-551/PERMUTEX® XR-5508 (available from Stahl) was used.

Sample Preparation

PET-POE: Coating and lamination process
A closed-weaved PET fabric was coated with the primer by a draw-down method, using a stainless bar, and then placed in an oven for 3 minutes at 120°C to remove solvents. The coated fabric was laminated together with the POE sheet using a compression molder at 115°C for 12 seconds with the compression force of 4 kN. Coating weight of the primer was targeted at 10 gsm.

PC-POE: Dispersion Coating
POE sheet was coated with the primer by a draw-down method, using a stainless steel bar, and then placed in an oven for 3 minutes at 120°C to remove solvents. The polycarbonate dispersion was then applied by a draw-down method and then further dried. The coating weight was controlled to target a thickness of approximately 5-7 µm.

Testing

Peel strength by ASTM F2256
The laminated samples were cut into 3 cm x 15 cm rectangular specimens. The peel strength was measured using an Instron testing frame using 180 deg peel mode with a crosshead speed of 300 mm/min. The average load (kgf) was recorded and the average peel strength (kgf/3cm) was calculated from at least 3 samples.

Abrasion Resistance by ASTM D4157
The abrasion resistance was measured using a CSI-4 Wyzenbeek oscillatory cylinder abrasion tester with the sample abraded against Cotton duck 10#. The head pressure was set to 13.4 N (3 lbf), and the specimen tension to 17.8 N (4 lbf).

ATR-FTIR analysis
To examine the failure of the peeled substrates, ATR-FTIR was carried out on the inner surface of both the fabric and POE film. For comparison, the dried adhesive was also measured by ATR-FTIR. Perkin Elmer Spectrum Spotlight 200 with Smart DuraSample®Diamond ATR was used for ATR-FTIR analyze of the samples and spectra were collected and analyzed using Nicolet Omnic 7.3 software.

Morphology SEM/STEM analysis
Cryo-Microtome for SEM: Specimens were cut out with a razor blade. The isolated pieces were trimmed to an appropriate size by DIATOME Trimming knife and polished using a DIATOME CRYO 35° diamond knife at -100°C on a Leica UC6 microtome equipped with an FC6 cryo-sectioning chamber. Ruthenium Tetraoxide Staining: The stain solution was prepared by mixing 0.2 gram of RuCl3.5H2O with 10 milliliter of a 5% v/v NaClO in water. Samples for block staining were glued to the glass slide with double side tape and then put into a vial containing the prepared staining solution. The samples were vapor stained overnight at ambient temperature. The stained samples were rinsed with DI water and re-polished at -100°C.

Scanning Electron Microscope (SEM): The re-polished block surfaces were loaded into a Nova Nano630 SEM and observed by Back scattering Electron (BSE) detector at an accelerating voltage of 5 KV, working distance around 6.5 mm and spot size of 5.

Results and Discussion

PET Fabric to POE Lamination

Polymer-film coated fabrics can be used to improve the durability and haptics of laminates for many consumer and industrial applications. To expand the use of polyolefin sheets, the lamination of PET fabrics on the top or within the sheet can improve the tensile strength and creep resistance; as well as modifying the appearance and surface characteristics of the sheet.

To improve the adhesion of a PET fabric to a polyolefin elastomer, an adhesion primer was coated onto the surface of the PET fabric using a draw-down procedure. The primer solution was prepared by dissolving 10 % of a MAH-modified polymer. The primer solution was then applied to the PET fabric and subsequently dried. The modified fabric was then heat laminated to the polyolefin sheet for further testing.

In this study, four adhesion primers were prepared with polymers containing different levels of MAH-functionality (refer to Table 1). These primers were coated onto the fabric to achieve a target coating weight of 10 gsm and then laminated to the POE sheet.

Figure 1 shows the effect of having MAH-functionality in the adhesion primer on the peel strength between the PET fabric and POE substrate. Primer A, having no MAH-functionality, resulted in a peel strength similar to having no primer added. However, as the level of MAH-functionality increased (from Primer B, low level to Primer D, high level), the peel strength increased. The peel strength was highest, at the highest level of MAH to reach
a peel strength value of 2.7 kgf/3cm which is an acceptable strength for some coated fabrics.

To further improve the bonding strength, an additional 2K approach was attempted with the addition of an isocyanate crosslinker to the existing primer solutions.

Figure 2 shows the effect of adding 5 wt% of the isocyanate crosslinker to the same primer formulations based on its solids. The effect of the crosslinker addition resulted in increased peel strength. The addition of the crosslinker to primer A that contained no MAH, showed an increase to 3 kgf/3cm. However, in combination with MAH-functionality, the bonding increased to a peel strength of greater than 6 kgf/3cm, with the highest level close to 8 kgf/3cm with Primer D.

To test the bond stability, the samples prepared with the cross-linker were aged at room temperature for one week and the peel strength measured after 1, 3, and 7 days (refer to Table 3).

Table 3 – PET-POE Bond Stability (with crosslinker)

<table>
<thead>
<tr>
<th>Samples</th>
<th>0 day</th>
<th>1 day</th>
<th>3 day</th>
<th>7 day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>B-Low</td>
<td>5.9</td>
<td>6.2</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>D-High</td>
<td>5.5</td>
<td>5.8</td>
<td>6.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Figure 3 shows the peel strength versus time for samples tested over a one week period. It was observed that the peel strength increased slightly to reach a maximum strength after one week; this behavior was expected as the isocyanate crosslinker continued to cure. However, the trends show that both the fabric primed with Primer B (low MAH-functionality) and Primer D (high MAH-functionality) reached the same peel strength level after 7 days; the data also suggests that the fabric primed with Primer B reached a plateau after 3 days while Primer D continued to increase until 7 days.

To further understand the failure mechanism of the samples, visual inspection and ATR-FTIR analysis was used. Inspection of the samples coated with Primer B,C,D without isocyanate crosslinker (Figure 1) showed cohesive failure with residual adhesive on both the POE and PET sides. Figure 4 shows the ATR-FTIR composition of the surfaces of the failed substrates. The scans of the peeled POE and PET surfaces are almost identical, similar to the spectrum of the adhesive we used. They have the characteristic C=O stretching (from the anhydride groups) and C-H stretches of polyolefins. However, samples coated with Primer B,C,D with the isocyanate crosslinker (Figure 2 and 3) displayed substrate failure with the breakage of the POE film.
**Polar Coating Adhesion to POE**

Coatings applied to polyolefin substrates can be used to improve the abrasion resistance of polyolefin laminates. To improve the abrasion resistance of a polyolefin sheet, an abrasion resistant coating (such as PC or PU) can be applied to the surface to increase its hardness and/or reduce its coefficient of friction.

To improve the abrasion resistance of a polyolefin sheet, a PC dispersion was coated directly onto the polyolefin surface using a draw-down procedure. The primer solution was prepared by dissolving 5% of both a mono-functional modifier containing MAH and a bi-functional modifier containing both MAH and chlorine functionality (refer to Table 2). The polyolefin sheet with its applied primer solution was then dried and then the PC dispersion was applied.

Figure 5 shows the effect of the adhesion primer on the abrasion resistance of the POE sheet with PC coating. Without any adhesion primer, the abrasion resistance was poor and less than 5,000 cycles were reached. With the addition of Primer E (with MAH functionality only), the abrasion resistance increased and 20,000 cycles were reached. However, with the addition of Primer F (containing both MAH and Cl functionality), the abrasion resistance increased dramatically and 100,000 cycles were reached.

To further understand the failure mechanism, SEM micrographs were taken of the specimens before and after the abrasion testing.

Figure 6a shows that without the adhesion primer, after testing, the PC coating is damaged and removed to the point where very little was left.

Figure 6b shows that with the addition of the adhesion primer, after testing, the PC coating remains with about 60% of the thickness remaining and the primer layer remaining in-tact.
the highest abrasion resistance was achieved with the medium concentration; it is suspected that if the coating layer is too thick, the primer layer will fail adhesively along with the PC coating.

![Figure 7 - PC-POE Adhesion: Effect of Primer Concentration](image)

Conclusions

This study described the development of adhesion primers to promote and improve the bonding of a polar material to a polyolefin elastomer substrate. Two bonding examples were shown to adhere a PET fabric to a POE sheet and a PC coating to a POE sheet.

In the PET-POE example, the application of an adhesion primer that contains MAH-functionality, significantly increased the peel adhesion between the two substrates. The bonding level could also be further improved with the addition of an isocyanate crosslinker to reach a maximum bond strength after one week.

In the PC-POE example, the application of an adhesion primer that contains both MAH and chlorine functionality significantly increased the adhesion between the PC coating and the POE substrate to improve the abrasion resistance.

Overall, a combination of a surface adhesion primer and the application methodology can be an effective solution to provide the needed bonding. Such technology can be further applied to resolve the adhesion challenges of polyolefin elastomers to engineering plastics such as PET, PC, PU, and PA.

References


