STRUCTURE-PROPERTY RELATIONSHIPS AND APPLICATIONS OF NOVEL FLEXIBLE TPO BASED ON BLENDS OF DEVELOPMENTAL PERFORMANCE ELASTOMER AND POLYPROPYLENE

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Abstract

Blends of developmental performance elastomers (DPE), produced by INSITE™ technology, and polypropylene exhibit a superior balance of flexibility and heat resistance. These blends provide a new family of flexible TPO that can be engineered to meet performance requirements of many applications. Generalized blend design strategies for flexible TPO based on thermodynamic considerations are reviewed. Thermal, dynamic mechanical and tensile properties of the blends will be presented. The utility and potential applications of these blends will be highlighted.

Introduction

Flexible thermoplastic polyolefins (f-TPO) constitute an important class of materials due to its unique balance of flexibility and heat resistance. These materials are generally a physical blend of polypropylene and olefinic elastomers. They can be produced via an in-reactor process or melt compounding process. Due to the complexity involved in the catalyst and process technology for making reactor f-TPO [1], there are only a few commercial grades available with relatively limited modulus offering and melt flow rate grades. Flexible TPO produced via the melt compounding route allows tailoring of properties by independently controlling the molecular weight, composition and type of the blend components. However, these materials generally do not exhibit as good flexibility and heat resistance balance as the commercial reactor f-TPO. This difference is primarily related to the compatibility difference between the commercially available elastomer and the reactor elastomer with polypropylene. The special elastomer used in the commercial reactor f-TPO is very compatible or nearly melt miscible with polypropylene. These unique elastomers cannot be easily produced and isolated with the conventional PP catalyst and process technology.

Recently, the Dow Chemical Company developed novel developmental performance plastomers (DPP) and developmental performance elastomers (DPE), (formally referred to as propylene-ethylene copolymers), with a high degree of isotacticity and with high molecular weight [2-3]. These materials exhibit relatively narrow molecular weight distribution and unique micro-structures.

These new copolymers have comonomer distributions that are very different from copolymers made with traditional Ziegler-Natta (Z/N) catalysts or metallocene catalysts. Because of the composition and unique comonomer distribution, these copolymers, depending on comonomer content, are melt miscible or very compatible with polypropylene over a broad range of blend composition. Flexible TPO with excellent flexibility and heat resistance balance can be engineered by combining DPE with polypropylene. In this contribution, we will focus on the properties and potential applications of the new family of f-TPO based on blends of DPE and polypropylene.

Experimental

The blend components were first dry blended and then fabricated into films on a Haake 25-mm twin screw extruder equipped with a TPI Tape Postex with a 15 cm wide sheet die. The extruder operated at about 200 °C and 3.5 MPa. A Conair Tempro press was used to flatten out the sheet after the film rolled out from the chill roll. The sheet thickness was about 1 mm.

For compression molding tests, the samples were melted at 190°C for 3 minutes and compression molded at 190°C under 5.5 MPa pressure for 2 min. The molten materials were then quenched in a press equilibrated at room temperature.

Thermal mechanical analysis (TMA) was used to determine the upper service temperature. Samples were run in a thermal mechanical analyzer (Perkin-Elmer TMA 7 series) scanned at 5 C/min and a load of 1 Newton. The samples were compression molded into 2 mm thick films.

Ultimate tensile strength was determined in accordance with ASTM-C412, in the machine direction. Tensile modulus (2% secant) was measured in accordance
with ASTM-D882, in the machine direction. The samples were 1 mm thick extruded films.

Brittleness point was determined in accordance with ASTM-D-2136. The samples were 1.3 mm thick compression molded films.

Dynamical mechanical spectroscopy was run on a Rheometric Scientific Ares II at a constant frequency of 10 rad/sec. The temperature was ramped at 5°C/min from -100°C to about 200°C. All samples were run in rectangular torsion mode and with automatic adjustments for strain to maintain constant stress with increasing temperature. The specimens were cut into rectangles 1.5 mm thick by 10 mm wide and approximately 45 mm long.

Melt rheological testing was performed on a Rheometrics RMS-800 at 190°C over a frequency range from 0.01 or 0.1 to 100 rad/s. Parallel plates (25 mm) were used in all measurements. A strain of 1% was set for all samples with no automatic adjustments for strain to maintain constant stress with increasing temperature.

Atomic Force Microscopy (AFM): sections were collected from the sample material using a Leica UCT microtome with a FC cryo-chamber operated at -80°C. A diamond knife was used to section all sample material to a thickness of 120 nm. Sections were placed on freshly cleaved mica surfaces, and were mounted on standard AFM specimen metal support disks with a double carbon tape. The sections were examined with a DI NanoScope IV Multi-Mode AFM, in tapping mode with phase detection. Nano-sensor tips were used in all experiments.

Blend Design Strategy

Fundamental to the design of f-TPO is the ability to control the morphology of the blends and the thermal transitions of the individual component to yield an optimal balance of flexibility and heat resistance. To achieve this balance, the blend should exhibit very fine phase dispersion and the PP should be the continuous or the co-continuous phase. On the basis of the solubility parameter balance, the blend should exhibit very fine phase transitions of the individual component to yield an optimal balance of flexibility and heat resistance. To achieve this balance, the strain should be the continuous phase or the co-continuous phase for strain to maintain constant stress with increasing temperature.

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Results and Discussion

The modulus-composition dependence for the DPE-RCP blends and POE (0.863 g/cc density EO)-RCP blends is shown in Figure 1. Both the DPE and POE have similar levels of crystallinity. At an equivalent level of elastomer incorporation, the DPE is much more effective at reducing the modulus of the blends as compared to the POE blends. This is consistent with the Kerner-Nielsen model prediction [7] in which the modulus of a highly compatibilized (small phase dispersion) blend is predicted to be lower than that of a well phase separated (large phase dispersion) blend.

While the DPE blends yield a more flexible material, often a balance of flexibility and heat resistance is so critical to the performance of f-TPO. Heat resistance, generally expressed as upper service temperature, can be measured by a number of techniques. High temperature tensile testing, modulus as measured by dynamic mechanical spectroscopy (DMS), softening temperature as determined by Vicat temperature measurement, penetration resistance as probed by thermal mechanical analysis (TMA) have been used to correlate the heat resistance of material response. Depending on the nature of the application, different measurement may be used to quantify the upper service temperature. For very flexible
applications, penetration temperature as determined by TMA has been shown to correlate well with upper service temperature. In contrast to the Vicat temperature which is a single penetration measurement, TMA yields the entire penetration-temperature profile. The variation of the TMA (1mm penetration) temperature with the tensile modulus for the DPE and POE blends are illustrated in Figure 2. For an equivalent modulus, it can be clearly observed that DPE blends exhibit a higher upper service (TMA) temperature than the corresponding POE blends.

The difference in the flexibility-heat resistance balance between the DPE and POE blends can be rationalized based on the differences in compatibility and hence the phase morphology of the blends. Figure 3 shows the phase morphology of the blends obtained via atomic force microscopy. The dark region represents the elastomer phase and the lighter region denotes the PP phase. The solubility parameter differences, estimated based on Graessley’s scheme [6], for the DPE-RCP and POE-RCP blends are illustrated in Table 1. It can be seen that the DPE-RCP blends are very compatible as reflected by the very small difference in the solubility. This is very consistent with the very fine domains suggesting that the interfacial tension between the phases is very small. In contrast, the POE/RCP blends exhibit much coarser dispersion indicative of incompatibility. This behavior is consistent with the relatively large solubility parameter difference between the POE and RCP.

It is known that the modulus of a multi-phase system is strongly dependent on the size, shape/geometry and volume fraction of the dispersed phase [8]. For a fixed crystalline morphology (e.g. crystallinity level and crystalline structure), the modulus of semi-crystalline blends generally decreases with decreasing size of dispersed phase. In the case of the DPE-RCP blends, the large modulus reduction could also be related to the possible change in the aspect ratio of the crystals resulting from changes in crystallization. This potential change in the crystal structure is related to the very good blend compatibility. Because of the unique comonomer distribution of the DPE, it is believed that the DPE could co-crystallize with the RCP. This mechanism could also contribute to the superior heat resistance observed in the DPE blends.

**DPE-PP Blends versus Reactor f-TPO**

The TMA profiles for DPE blends and a commercial reactor f-TPO (CRf-TPO) are displayed in Figure 4. The DPE blends are designed to have a similar modulus as the CRf-TPO. It can be seen that the DPE blends are more resistant to penetration over a very broad temperature range as compared to the CRf-TPO. The storage modulus as measured by DMS for a DPE blend and CRf-TPO is shown in Figure 5. The DPE blend has essentially the same modulus-temperature dependence as the CRf-TPO up to the melting point of the polypropylene. The higher modulus observed in the flow region for CRf-TPO merely reflects that the CRf-TPO has a higher MW relative to the DPE blend.

Upon close examination of the DMS property of the DPE blend and the CRf-TPO reveals that the CRf-TPO is consisted of three distinct phases. The tan δ plots for these materials are shown in Figure 6. The Tg of the main elastomer phase for the DPE blend and CRf-TPO is essentially identical. However, the CRf-TPO clearly shows a distinct shoulder at around -50 °C which is a signature for a second elastomer. This clearly indicates that this particular CRf-TPO is a blend of two elastomer and RCP. As discussed earlier, the low temperature elastomer is required to impart better low temperature toughness to the blend.

The low Tg transition can be engineered into the DPE blends by introducing either a second elastomer such as a POE or by replacing the RCP with ICP. Figure 7 clearly shows that the Tg of the POE phase or the EPR phase in the ICP is essentially the same as the low Tg elastomer of CRf-TPO. The low temperature toughness of the DPE blends and CRf-TPO is compared in Figure 8. The brittleness point of the DPE-RCP blend is about -30 °C which nicely scales with the Tg of the DPE. Depending on the level of the POE in the DPE-RCP blends, the brittleness point is similar or even lower than that of the CRf-TPO. Another route to enhance the low temperature property of DPE blends is to replace the RCP with ICP. It can be seen from Figure 8 that the brittleness temperature of the DPE-ICP blend is comparable to that of the CRf-TPO.

The tensile strength of the DPE blends and CRf-TPO is shown in Figure 9. It can be seen that the DPE blends generally exhibit better tensile strength than the CRf-TPO even though the overall MW of the DPE blends is lower. The difference in viscosity between the DPE blends and CRf-TPO is depicted in Figure 10. On the basis of the viscosity profile, the DPE blends can be designed to have lower MW and hence better processability but better tensile properties as compared to CRf-TPO. This difference is probably related to the relatively narrow MWD of the DPE blends as compared to the relatively broad MWD of the CRf-TPO. It is well known that the low MW species generally exert a detrimental effect on the mechanical properties of polymers.

**Potential Applications**

Due to the unique combination of flexibility-heat resistance-low temperature toughness of the new DPE-PP blends, these novel materials could find utility in many demanding flexible applications currently served by high performance thermoplastic elastomers and commercial
reactor f-TPO. Depending on the composition and MW of the DPE and PP, novel f-TPO could be designed to meet or exceed the property balance of commercial reactor f-TPO. The DPE-PP blends offer unprecedented degree of formulation flexibility for f-TPO which enables custom design of materials to meet specific application needs.

Single-ply TPO roofing, artificial leather and other coated fabrics, soft touch compounds for consumer and automotive articles, and calendared or extruded films and sheet are only a few examples of the potential applications of the new DPE-based f-TPO. For example, DPE-RCP blends offer exceptional good balance of optics, flexibility and heat resistance which render these materials suitable for flexible PVC and styrenic block copolymer replacement for clear applications such as calendared films and sheets.

### Conclusions

A new family of developmental performance elastomer (DPE) with unique compatibility to polypropylene provides a new generation of flexible TPO (f-TPO). Blends of DPE and PP exhibit a unique balance of flexibility-heat resistance-low temperature toughness that is superior to currently available commercial compounded f-TPO. It has been demonstrated that these novel materials can be engineered to meet or exceed the property profile of commercial reactor f-TPO. Due to their robust design, the DPE-PP blends offer unprecedented degree of formulation flexibility for f-TPO which enables custom tailoring of properties to meet specific application needs.

### References


### Acknowledgements

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<table>
<thead>
<tr>
<th>Blend</th>
<th>$10^3(\Delta \delta)^2$, J/cm$^3$</th>
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<tbody>
<tr>
<td>DPE-RCP</td>
<td>9.2</td>
</tr>
<tr>
<td>EO-RCP</td>
<td>140.6</td>
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Table 1: Square of solubility parameter difference $(\Delta \delta)^2$ for DPE-RCP and EO-RCP (3 wt% ethylene RCP).

![Figure 1: Tensile modulus-composition dependence of DPE-RCP and POE-RCP blends.](image)

![Figure 2: Correlation between heat resistance, as measured by 1 mm penetration TMA temperature, and tensile modulus for DPE-RCP and POE-RCP blends.](image)
Figure 3: Blend morphology of POE-RCP and DPE-RCP blends. The dark region is the elastomer phase and the light region is the PP phase.

Figure 4: TMA plots for DPE-PP blends and a commercial reactor f-TPO (CRf-TPO).

Figure 5: Storage modulus of DPE-RCP blend and a commercial reactor f-TPO (CRf-TPO).

Figure 6: Glass transition behavior of DPE-RCP blend and a commercial reactor f-TPO (CRf-TPO).

Figure 7: Glass transition behavior of DPE blends and a commercial reactor f-TPO (CRf-TPO).

Figure 8: Brittleness temperature of DPE blends and a commercial reactor f-TPO (CRf-TPO).
Figure 9: Tensile strength of DPE blends and a commercial reactor f-TPO (CRf-TPO).

Figure 10: Viscosity profiles for DPE blends and a commercial reactor f-TPO (CRf-TPO).