

Tailoring HM Properties With Intra-APAO Blending

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The most important single component in a hot melt adhesive (HMA) or sealant formulation is the polymer. It is the backbone or strength component of the HMA. This article will show how blending two Rex-tac (RT) amorphous polyalphaolefins (APAO) can produce products with properties that meet specific requirements such as needle penetration, while having little effect on other properties such as the melt viscosity.

The APAO, which include atactic polypropylene (APP), are used customarily in the hot melt adhesives and sealants industry in such applications as packaging, assembly operation of molded carpet components for automotive use, assembly of multi-wall bags, window sealants for commercial construction and a variety of non-woven HMA applications. They encompass a group of usually low molecular weight polyolefins — melt viscosities (MV) in the 100-10,000 cps range at 190°C — which are obtained by a coordination polymerization (Ziegler-Natta) process. The APPs are a by-product in the production of isotactic crystalline polypropylene using first generation catalysts, but with the development of new catalysts that are highly active and stereospecific, less atactic polymer is produced. As a result, APP supply from polypropylene plants using standard first generation Ziegler-Natta catalysts is decreasing as commercial plants continue to convert to high activity catalysts. Consequently, a few companies now are producing APAO directly, which means more precise control of product properties.

There are three distinctive product types of RT on-purpose amorphous polyalphaolefins (APAO), made by direct reactor synthesis:

- homopolymers of propylene;
- copolymers of propylene and ethylene; and
- copolymers of propylene and 1-butene.

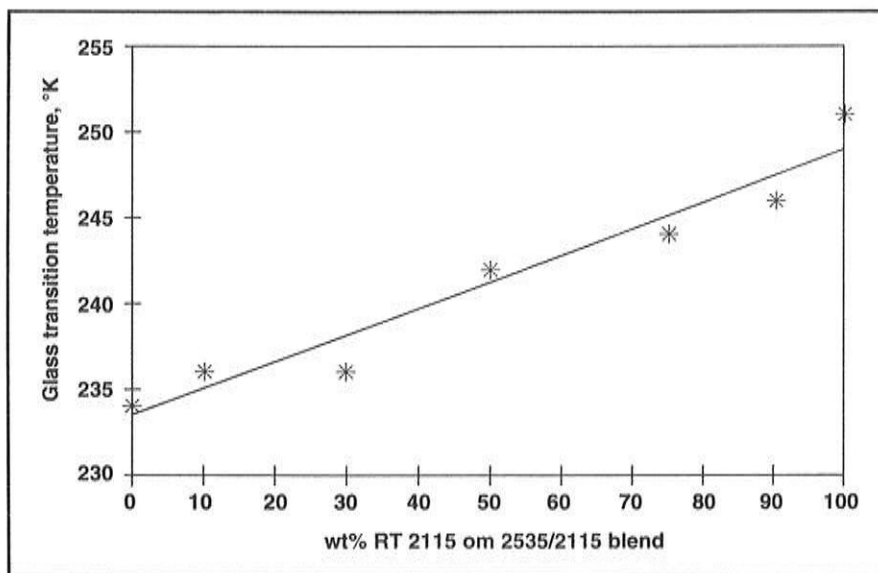


Figure 1. Composition vs. glass transition temperature profile of a 2535/2115 blend.

Proper design of the process of synthesizing the amorphous polyolefin, i.e. proper choice of the catalyst system and of comonomers, results in products that have well-defined product properties such as melt viscosity, softening point, needle penetration, embrittlement temperature and open time.

Due to the limited number of RT APAO product types that are produced, however, a formulator might be in need of a particular product that has some specific properties of melt viscosity, needle penetration or softening point, not available as a neat product. With that in mind, we have carried out a program to establish how blending two different RT APAO determines the final properties of the blends.

Experimental

The characterization of the blends reported in this work required the use of techniques that are widely used in the

HMA industry by suppliers, formulators and end-users. Test methods used include needle penetration — ASTM D-1321; softening point — ASTM E-28; melt viscosity — ASTM D-3236; open time — Rexene method; SAFT, TMHM-0232; and glass transition — ASTM D-3417.

Several methods are used to determine the glass transition of a polymer material; the mechanical/rheological, the calorimetric, the dilatometric and the dielectric are the most commonly used. The calorimetric method has been gaining wide acceptance; the most common instrument used is the differential scanning calorimeter (DSC).

The following paragraphs include some brief definitions of these characterization methods.

Melt Viscosity. The melt viscosity (MV) is the most distinctive property because it determines the degree of wetting or penetration of the substrate by the adhesive; it gives an indication of

the processability of the adhesive.

Needle Penetration. With thermoplastics and elastomers, hardness often is used as a simple measure of stiffness. The needle penetration (NP) indicates the resistance to deformation (or hardness) of the polymer.

Softening Point. The softening point of a polymer, usually referred to as the Ring and Ball Softening Point (RBSP), is important in hot melt adhesives because it gives an indication of the heat resistance. RBSP and glass transition temperature define the temperature range where the HMA can be used without softening or becoming brittle.

Open Time. Open time (OT) can be defined as the time between applying a hot melt adhesive and the time prior to the hot melt losing its wetting ability because of solidification and crystallization.

SAFT. The Shear Adhesion Failure Temperature (SAFT) determines the temperature at which specimens bonded with HMA delaminate under static load in shear mode.

Results

Intra-APAO Miscibility. The most commonly used method for establishing miscibility in polymer-polymer blends is through determination of the glass transition temperatures of the blends vs.

those of the pure, unblended components. A simple definition for glass transition temperature may be that temperature below which the polymer is glassy and above which it is rubbery (1). A miscible polymer blend will exhibit a single glass transition temperature (Tg) between the Tgs of the pure components.

Tgs were determined by DSC for blends of homopolymer RT 2115 and high ethylene copolymer RT 2535. The thermograms of each blend showed only

a single Tg. Figure 1 shows a plot of composition vs. glass transition temperature for the blends. These blends were chosen because the difference in the Tg of the pure components is the widest, ca. 17°C of all our APAO. This is important because the glass transitions appear as somewhat broadened inflection points so the greater the difference in the Tgs, the higher the resolution. Nevertheless, the results indicate that the blends of 2115 and 2535 are miscible in all proportions, and this should be ex-

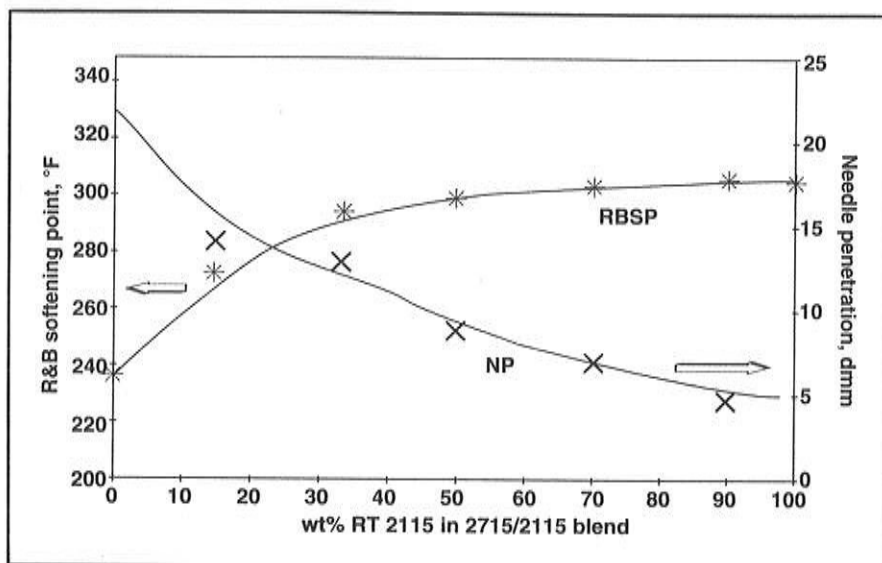


Figure 2. Effect of RT 2115 on the RBSP and the needle penetration of an RT 2715/RT 2115 blend.

Table I — Physical Properties for the RT 2715/RT 2115 Blend

wt % RT 2115 in 2715/2115 blend	0	15	33	50	70	90	100
R&B SP, °F	235	273	295	300	306	307	308
NP, dmm	22	14	13	9	7	5	5
SAFT, °F	173	204	235	245	257	265	269

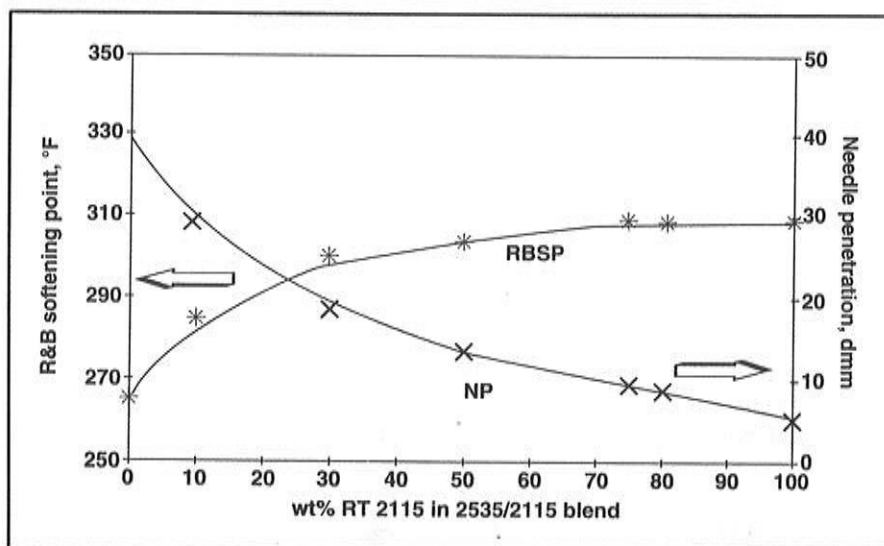


Figure 3. Effect of RT 2115 on the RBSP and the needle penetration of an RT 2535/RT 2115 blend.

pected given that both components are hydrocarbon polymers for which the difference in the solubility parameters, δ , is less than 0.5 (cal/cm³)^{1/2} (2). We can safely state that all our APAOs are miscible with each other, in all proportions.

Composition Effect on NP, RBSP and MV. When the low softening point butene copolymer 2715 (MV, 1500 mPas), which has a higher needle penetration, is blended (diluted) with the hard, high softening point 2115 homopolymer (MV, 1500 mPas), the effect is a decrease in the needle penetration, with the blend becoming harder. The NP at any composition is well described by the following expression:

$$\ln NP = 2.98 - 0.0146 \text{ wt\%}$$

where $\ln NP$ is the natural logarithm of the NP, and for which the linear regression coefficient r was found to be -0.988 . On the other hand, the softening point quickly increases so that at a 50:50 blend composition, it already has reached the softening point of the harder homopolymer. Figure 2 shows plots for both the NP and the RBSP as function of the blend compositions, while Table I shows the corresponding values for NP and RBSP. As the two polymers are miscible, the softening point of the lower melting component is raised by the presence of the second component. This type of behavior is well known in the thermodynamics of blends (or alloys) that show liquid (molten) phase-solid phase miscibility, provided the interactions between the polymeric components are no stronger than the Van der Waals forces. The shape of the softening point vs. composition curve is similar to the build-up period in acceleration type coordination polymerization and the mathematical expression for this curve is somewhat more complex than for the NP vs. composition curve.

The former blend consisted of two components with the same melt viscosity of 1500 mPas. When blending is done with two components of different melt viscosities, as when homopolymer 2115 is added to a high ethylene, very soft copolymer (2535), the progressive addition of 2115 has an appreciable effect on the needle penetration with it steadily decreasing until reaching the value obtained for the pure RT 2115 component. As with the 2715/2115 blend, it is also possible in this case to describe the behavior of the NP as a function of blend composition by the following expression:

$$\ln NP = 3.588 - 0.019 \text{ wt\%}$$

for which the linear regression coefficient r is -0.995 . As was the case with the 2715/2115 blend, the softening

Table II — Physical Properties for the RT 2535/RT 2115 Blend

wt % RT 2115 in 2535/2115 blend	0	10	30	50	75	90	100
R&B SP, °F	265	286	298	303	308	308	308
NP, dmm	40	29	18	13	9	8	5
MV, mPa·s	3475	3075	2590	2225	1875	1800	1425

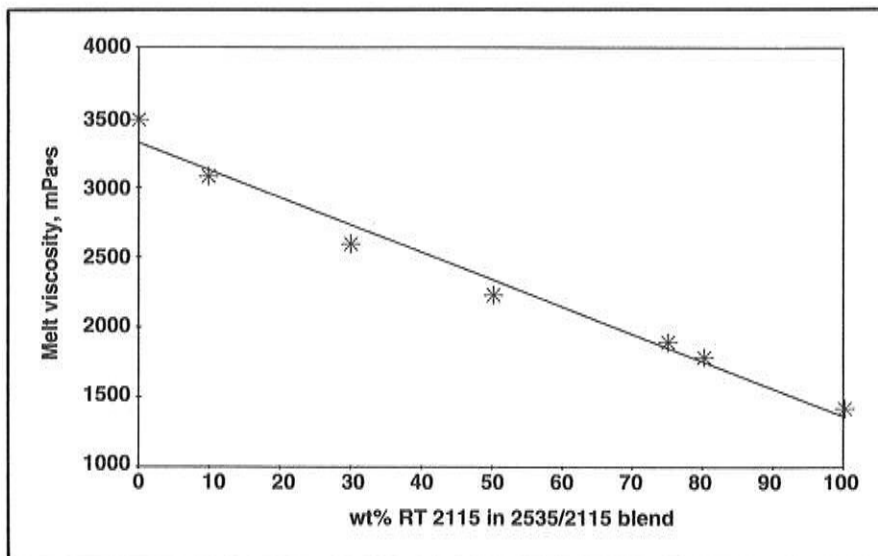


Figure 4. Effect of RT 2115 on the melt viscosity of an RT 2535/RT 2115 blend.

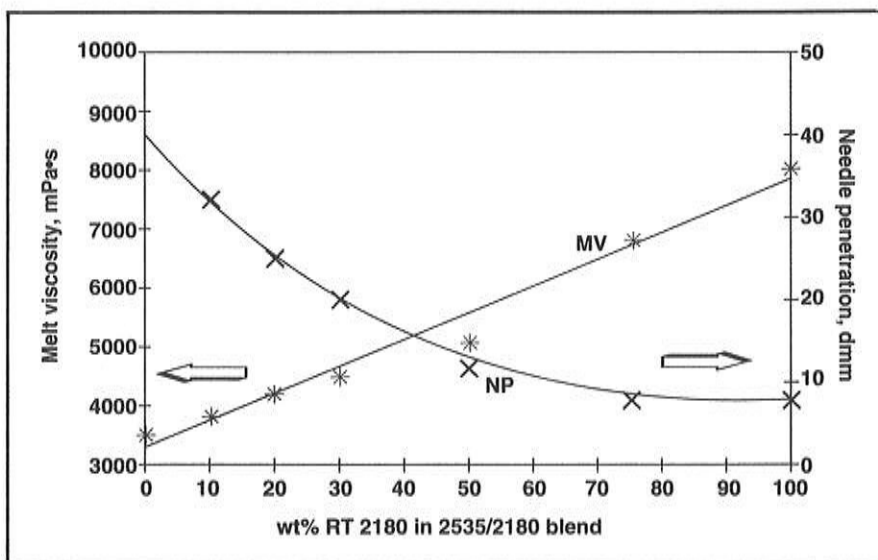


Figure 5. Effect of RT 2180 on the melt viscosity and the NP of an RT 2535/RT 2180 blend.

point of the blend increases rapidly with the addition of small quantities of 2115, reaching a plateau at a blend composition of about 50/50. Figure 3 shows plots for both the NP and the RBSP as function of the blend compositions, while Table II shows the corresponding values for NP and RBSP. Again, addition of small quantities of 2115 cause large initial changes both in the NP and in the softening point. On the other hand, the melt viscosity experiences a

more linear change with concentration of modifier (Figure 4).

Similar behavior has been observed for several other intra-APAO blends, for example small additions of low ethylene RT 2215 to high ethylene RT 2535 cause relatively large initial changes both in the NP and in the softening point. Because the difference in the NP and the RBSP between 2215 (NP, 20 dmm; RBSP, 290°F) and 2535 is not as large as when 2115 is used, the changes

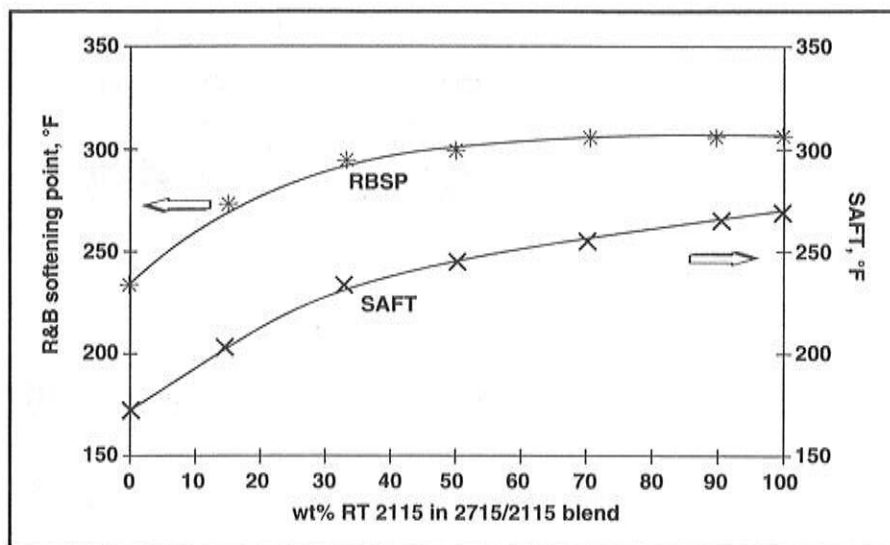


Figure 6. Effect of RT 2115 on the RBSP and the SAFT of an RT 2715/RT 2115 blend.

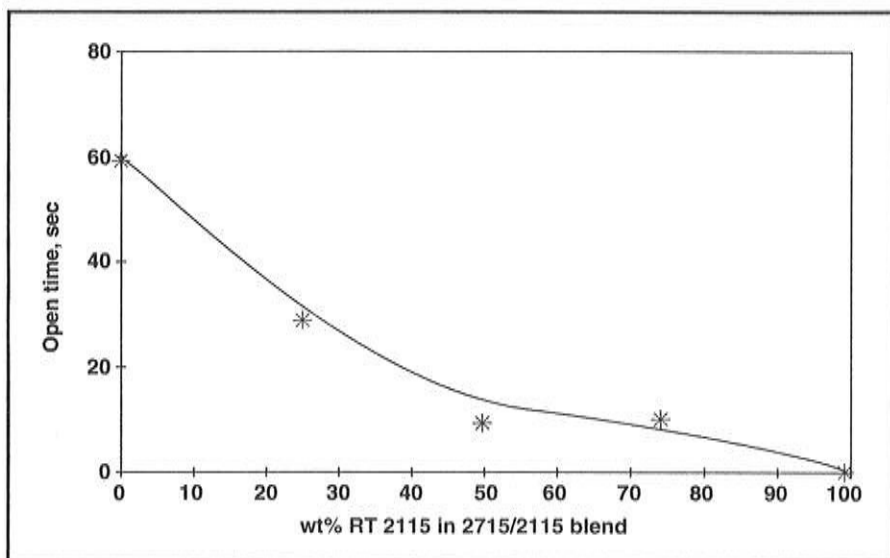


Figure 7. Effect of RT 2115 on the OT of an RT 2715/RT 2115 blend.

are not as steep. Figure 5 illustrates how the melt viscosity of a blend of RT 2535 and RT 2180 changes in a linear fashion as the concentration of 2180 in the blend increases, while the NP shows a logarithmic behavior, becoming harder as more 2180 is added to the blend. Even though it is not shown in the figure, the RBSP, as was the case for other blends, almost reaches a plateau at a 50:50 composition.

Composition Effect on SAFT and OT. We recently have shown (3) that the SAFT of the neat APAO is directly dependent on APAO softening points, in other words, the homopolymers having the highest softening points show the highest SAFT. Additionally, as the softening point of the APAO decreases, so does the shear adhesion failure temperature. Not unexpectedly, a similar trend has been observed for intra-APAO blends. In a blend formulated with the components that show the wid-

est difference in SAFT, RT 2115 and RT 2715, the SAFT increases as the concentration of 2115 in the blend increases (Figure 6); the shape of the curve is similar to the shape of the composition vs. softening point for the blend, as has been shown in Figure 2. Again, a small amount of homopolymer has a large initial effect on the SAFT of the lower SAFT component, the butene copolymer.

One important variable that affects the open time of an HMA is the fraction of rapidly crystallizable polymer. If an otherwise amorphous polymer contains a small fraction of crystallizable polymer, its OT will decrease. The effect of adding RT 2115 (this homopolymer contains up to 20 wt% of a fraction that is insoluble in boiling heptane), with no measurable open time, to RT 2715, which exhibits an open time of 60 sec, is to decrease the OT of the blend (Figure 7). The drop is quite steep

Since the two polymers are miscible, the softening point of the lower melting component is raised by the other.

with the addition of small amounts of 2115. However, 2115 adds strength to the blend and because it solidifies/crystallizes so fast, we should expect that the set time, which can be defined as the time it takes for an adhesive to solidify and form a destructive bond, will be improved.

Conclusion

The results presented in this article intend to show the benefits of intra-APAO blending when a product with specific characteristics and properties is not available. We have shown that the desired composition with the unique properties a HMA formulator or end-user is looking for can be obtained directly from the plots of composition vs. property. Moreover, provided an expression is known for the change of a particular property with blend composition, it is also possible to obtain the desired composition, as we have shown for the needle penetrations and for the melt viscosities. This widening of the properties can be achieved successfully because, as already noted previously, the reactor-made APAO can be produced with tightly controlled physical properties.

Further work in the rheological properties of intra-APAO blends, which will determine with higher precision their Tgs along with the storage and loss moduli (with the intent to determine, for example, the "window of application" of the blend), currently is being undertaken.

Acknowledgment

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