

New APAO Offer Expanded Properties for HMA Applications

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The most important component in a hot melt adhesive (HMA) or sealant formulation is the polymer. It is the backbone or strength component of the hot melt. HMAs are a fast-growing segment of the amorphous polyalphaolefins (APAO) market. They are a formulation of a thermoplastic, tackifier resin, a wax, a thermal stabilizer and sometimes a modifier. They are used in a variety of industries including packaging, book binding, nonwovens and automobile assemblies. Important polymer parameters that allow for successful use of a hot melt adhesive in these applications are low melt viscosity, good cohesive strength, wettability of the substrates and a broad application window.

Amorphous polypropylene (APP), still used in some HMA formulations, is obtained as a by-product of polypropylene produced using old Ziegler-Natta coordination polymerization technology. With the advent of newer catalyst and process technologies, it is possible to produce on-purpose, amorphous polyalphaolefins that have a wide range of closely reproducible properties such as Brookfield melt viscosity, softening point, needle penetration and open times. Other polymer properties, such as tensile strength or rheology, contribute in giving a better picture of how a polymer behaves when used as a component in an HMA or sealant formulation.

In the past, Rexene has presented data for Rextac (1) amorphous polyalphaolefins (RT APAO), describing a broad range of properties and characteristics (2,3). To extend the range of properties available in its commercially available products, the company also has presented data on the properties of "intra-APAO" blends (4).

Moreover, Rexene recently has presented rheological data for RT APAO and for a few blends of APAO with styrenic block copolymers of common

use in the hot melt adhesive industry (5). Rheological data is important, as polymeric materials are inherently viscoelastic. Their responses to deformation can be determined by dynamic mechanical analysis (DMA). Dynamic oscillation over a frequency range is used to determine the storage modulus G' as a measure of elasticity (or the energy stored by an adhesive). A low elasticity is desirable during application, but a high value is favorable during end-use. This parameter can be varied easily for a given polymer by adjusting the temperature of application.

Rexene has perceived a growing demand for APAO products that exhibit high tensile strength and a low soft-

Hot melt adhesives are a fast-growing segment of the amorphous polyalphaolefins (APAO) market.

ening point — low enough so that the polymers can be applied to temperature-sensitive substrates. In response to this demand, the company is introducing three new 1-butene RT APAO. Two of these show very high tensile strengths and storage moduli while having softening points lower than 200°F. The third does not have the unusually high tensile strength properties of the first two, but with a low softening point, it shows open times longer than 30 min.

The company also is introducing two new ethylene RT APAO that show higher tensile strengths and storage moduli than the commercially available RT 2500 series at similar ethylene contents; they also display a

broader range of application temperatures. The application temperature range is delimited by the glass transition temperature and the ring and ball softening temperatures.

All of these new developmental products have been produced in the company's pilot plant by combining the right set of conditions in the polymerization process (6).

Experimental

The characterization of the new products reported in this work required the use of techniques used widely in the HMA industry by suppliers, formulators and end-users. Test methods used include melt viscosity (ASTM D-3236); ring and ball softening point (ASTM E-28); needle penetration (ASTM D-1321); shear adhesion failure temperature, or SAFT (TMHM-0232); tensile strength (ASTM D-638); dynamic mechanical analysis (ASTM D-4440); glass transition temperature (ASTM D-3418); gel permeation chromatography, or GPC (ASTM D-3593, Rexene modified); and open time (ASTM D-4497, Rexene modified).

The following are brief definitions of these characterization methods:

Melt Viscosity. The melt viscosity is the most distinctive property, because it determines the degree of wetting or penetration of the substrate by the adhesive. It also gives an indication of the processability of the adhesive. Melt viscosities were determined using an RVT Brookfield Melt Viscometer at 190°C (375°F).

Softening Point. The softening point of a polymer, usually referred to as the ring and ball softening point (RBSP), is important in HMAs 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.

Needle Penetration. With ther-

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

Shear Adhesion Failure Temperature. SAFT determines the temperature at which specimens bonded with HMAs delaminate under static load in shear mode; it is another measure of heat resistance. The samples were prepared as Kraft paper strips 1 in. wide x 3 in. long and joined by a 1 x 1-in. adhesive bond area. They were heated in a circulating air oven at a heating rate of 60°F/hr.

Tensile Strength. One of the most informative testing methods for any material is the determination of its stress-strain curve in tension. Die-cut dumbbell-shaped samples were clamped in the jaws of an Instron 1125 Tensile Tester and elongated at a cross-head speed of 2 in./min. The values reported are the tensile strengths at break.

Dynamic Mechanical Analysis. DMA is a technique used to determine how a polymer responds when deformed. It can be used to better understand the role of polymers in HMA applications. DMA of the new products was carried out on a Bohlin Reologi AB rheometer. The modulus vs. frequency experiments were carried out using the Controlled Stress Rheometer. The samples, disks 25 mm in diameter and 3 mm thick, were prepared by compression molding around 2 g of RT APAO at 260°F. G' was determined using 25-mm parallel plates and a 3-mm gap. A frequency sweep was conducted, and the G' at 1 Hz read from the plot. The data reported for each experiment are the averages of at least two runs. From the rheogram at 25°C, it is also possible to obtain the dynamic viscosity.

Glass Transition Temperature. The glass transition temperature, T_g , is an important parameter to know before deciding on the application of a non-crystalline polymer. It can be defined as the temperature below which free rotations cease because of intramolecular energy barriers, or, alternatively, as the temperature that marks the onset of segmental motion. The T_g of the samples was determined by thermal analysis using a Perkin-Elmer DSC-2C at a heating rate of 10°C/min.

Gel Permeation Chromatography. GPC is one of the most powerful and versatile analytical techniques available for understanding and predicting polymer properties and performance. It is the only proven technique for characterizing the complete molecular weight distribution (MWD) of a polymer. Molecular weight determinations were conducted using a Wa-

Table I — Physical Properties of Commercially Available Ethylene RT APAO

Properties	Product type	
	2535	2585
Melt viscosity, mPA.sec	3500	8500
Ring and ball softening point, °C (°F)	129 (265)	129 (265)
Needle penetration, dmm	45	40
SAFT, Kraft-to-Kraft, °C (°F)	83 (182)	95 (203)
Tensile strength, MPa (psi)	0.35 (50)	0.35 (50)
Storage modulus at 1 Hz and 25°C, MPa	0.8	1.8
Glass transition, °C (°F)	-37 (-35)	-37 (-35)
M_w, M_n (K Daltons)	51, 11	62, 12
Open time, sec	60	60

Table II — Physical Properties of New Ethylene RT APAO

Properties	Product type	
	92005	92009
Melt viscosity, mPA.sec	7050	6700
Ring and ball softening point, °C (°F)	141 (285)	138 (280)
Needle penetration, dmm	10	20
SAFT, Kraft-to-Kraft, °C (°F)	120 (248)	112 (233)
Tensile strength, MPa (psi)	1.79 (260)	0.71 (103)
Storage modulus at 1 Hz and 25°C, MPa	8.3	3.4
Glass transition, °C (°F)	-47 (-53)	-47 (-53)
M_w, M_n (K Daltons)	94, 13	72, 11
Open time, sec	<10	<10

ters 150-C GPC on 0.1 wt% solutions of the polymers in trichlorobenzene at 140°C. The μ -Styragel column was calibrated using narrow molecular weight polystyrene standards. The elution peaks are unimodal showing a Gaussian distribution.

Open Time. Open time (OT) can be defined as the time between HMA application and the condition prior to the hot melt losing its wetting ability because of solidification and crystallization. Both the substrate and the strips are made of Kraft paper.

Results and Discussion

New Ethylene RT APAO. Table I shows the physical properties of commercially available ethylene RT APAO. Note the low tensile strength exhibited by the two copolymers. Among the RT APAO, these are the weakest and also the softest, as determined by their high needle penetration and their low storage moduli. Table II indicates the physical properties of the new ethylene RT APAO. Several properties show improvements. Significantly, the range of application temperatures has broadened by almost 20°C (36°F). In other words, the softening points have increased by 10-12°C, whereas the glass transition temperatures have decreased by an equivalent amount. The determination of the softening point of a polymeric material is like a single

creep test in tension combined with variable temperature, and it gives information of long-term dimensional stability. The glass transition temperature is determined primarily by the chemical composition and, in the case of copolymers, by the comonomer distribution in the polymer chains.

Compared to the RT 2500 APAO, the shear adhesion failure temperatures of the new RT APAO are 17-37°C higher, signifying that these new copolymers have a significantly higher heat resistance under static shear than the RT 2500 series APAO. However, these polymers show open times of just a few seconds and are also harder to penetrate, as indicated by a decrease of two to four times in needle penetration values. On the other hand, the degree of crystallinity — as determined by the DSC heats of fusion and the amount of boiling heptane insolubles, known as the long heptane insolubles — has changed little. In other words, change in the OT and NP values has not been induced by a higher degree of crystallinity in the new products.

The MWD (defined by the M_w/M_n ratio) of these new polymers is rather broad, ranging from 6.5-8.5. This range is slightly broader than the MWD range observed for the company's commercially available products, whose values range from 5-6. The apparent differences in these values are part of the changes in the properties of the

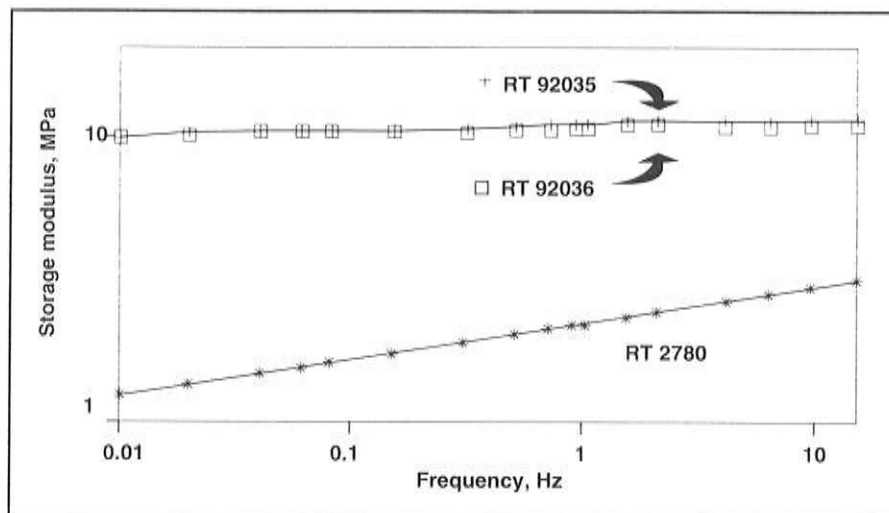


Figure 1. Storage modulus, G' , vs. frequency at 25°C for RT 2780, RT 92035 and RT 92036 APAO.

Table III — Physical Properties of Commercially Available 1-Butene RT APAO

Properties	Product type		
	2715	2730	2780
Melt viscosity, mPA.sec	1500	3000	8000
Ring and ball softening point, °C (°F)	107 (225)	107 (225)	107 (225)
Needle penetration, dmm	25	25	25
SAFT, Kraft-to-Kraft, °C (°F)	78 (173)	78 (173)	82 (180)
Tensile strength, MPa (psi)	0.56 (80)	0.61 (90)	No break
Storage modulus at 1 Hz and 25°C, MPa	3.4	3.2	2.1
Glass transition, °C (°F)	-23 (-9)	-23 (-9)	-23 (-9)
M_w, M_n (K Daltons)	40, 15	—	55, 18
Open time, sec	120	120	120

Table IV — Physical Properties of New 1-Butene RT APAO

Properties	Product type		
	92024	92035	92036
Melt viscosity, mPA.sec	4200	6150	11,500
Ring and ball softening point, °C (°F)	82 (180)	88 (190)	93 (200)
Needle penetration, dmm	28	5	5
SAFT, Kraft-to-Kraft, °C (°F)	66 (151)	77 (170)	79 (175)
Tensile strength, MPa (psi)	0.36 (52)	4.7 (675)	6.0 (875)
Storage modulus at 1 Hz and 25°C, MPa	3.7	10.6	10.7
Glass transition, °C (°F)	-39 (-38)	-39 (-38)	-39 (-38)
M_w, M_n (K Daltons)	83, 13	88, 11	125, 15
Open time, sec	1800	240	240

Table V — Physical Properties of Competitive APAO

Properties	Product type		
	Polymer A	Polymer B	Polymer C
Melt viscosity, mPA.sec	8000	3000	8000
Ring and ball softening point, °C (°F)	82 (180)	127 (260)	107 (225)
Needle penetration, dmm	15	12	20
SAFT, Kraft-to-Kraft, °C (°F)	71 (160)	97 (207)	88 (191)
Tensile strength, MPa (psi)	1.22 (177)	1.82 (264)	0.77 (111)
Storage modulus at 1 Hz and 25°C, MPa	8.8	10.2	4.2
Glass transition, °C (°F)	-25 (-13)	-20 (-4)	-30 (-22)
M_w, M_n (K Daltons)	66, 17	52, 14	70, 16
Open time, sec	900	15	55

new copolymers, induced by changes in the polymerization process, as mentioned above. The broad MWDs are expected generally for all polymers obtained with heterogeneous coordination polymerization catalyst systems.

Finally, the two most relevant properties that characterize the new RT amorphous polyalphaolefins are the storage modulus and the tensile strength. As highlighted in Table II, RT 92005 has a tensile strength as much as five times higher than that shown by the RT 2500 products, whereas RT 92009 shows only a twofold improvement in the tensile strength. Likewise, as highlighted in Table II, the storage modulus for RT 92005 is five to ten times greater (G' for RT 2535 and RT 2585 is 0.8 and 1.8 MPa, respectively), while RT 92009 has two to four times higher storage modulus.

All of the above changes were made with the right adjustment of the process conditions to synthesize these new products. The company's ability to continue making its traditional products is not affected at all.

New 1-Butene RT APAO. Table III shows the physical properties of the commercially available 1-butene RT 2700 series APAO. Of all the RT APAO polymers, these products show the lowest softening points. However, they also show low tensile strength for some applications.

Figure 1 shows a typical curve obtained in dynamic oscillation at a constant temperature of 25°C for RT 2780 and the new RT 92035 and RT 92036 APAO. It is immediately obvious that the new APAO have a much higher storage modulus than the RT 2780. Because the products are stiffer, their change in G' with the frequency of deformation is lower, which explains why the slope of their curves is less than the slope of G' vs. frequency for RT 2780. For RT 92036, the G' vs. frequency plot matches rather closely the plot obtained for RT 92035. For both products, there is a significant increase in the storage modulus compared to that of RT 2780. McLaughlin and Latham (7) reported that G' reaches a plateau at higher frequencies for higher molecular weight APPs. No such behavior was noted here in the materials studied.

Table IV shows the physical properties of the new 1-butene RT APAO. The copolymers have softening points from 180-200°F while still maintaining an acceptably high shear adhesion failure temperature; particularly RT 92035 and RT 92036 have SAFTs only a few degrees lower than the RT 2700 products. RT 92024 has storage modulus and tensile strength values similar to the company's commercially available RT 2700 APAO — the most important

differences being that it has a very long open time (longer than 30 min), a softening point of 82°C (180°F) and a glass transition temperature reduced by about 15°C (27°F).

In the case of RT 92035 and RT 92036, these new products are harder than the RT 2700 APAO. Again, as in the case for the new ethylene RT APAO, this change in the NP values has not been induced by a change in the crystallinity of the copolymers, because they do not have any measurable DSC heats of fusion and they are completely soluble in boiling heptane. These new products also show remarkably low glass transition temperatures, so that even though their softening points have been lowered, their low temperature flexibility has improved and their temperature of application is around 120-130°C, very similar to the temperatures of application of the commercially available RT 2700. As is the case for the new ethylene RT APAO, these 1-butene APAO also show MWDs in the range of 7-8.

The most relevant differences between the new products RT 92035 and RT 92036 and the current 1-butene RT 2700 APAO reside in the tensile strength and the storage modulus. Figure 2 shows a plot of tensile strength vs. a fictitious parameter designated "process changes" (arbitrary units, AU), and Figure 3 shows the changes in the storage modulus of the butene copolymers brought about by the same process changes. The intercept of the X and Y axis, the zero point, gives the tensile strength and G' for a typical commercially available RT 2700 series APAO. As the process changes increase, a region is reached where there is sudden change in the slopes of the tensile strength and G' curves and a small process change causes a rather large change in either property. For the tensile strength, this property reaches a maximum at some point past which any further change results in a decrease of that property. No such maximum has been observed for the storage modulus, which appears to have reached a plateau. The differences are clear in Figure 4, which compares the tensile strengths and storage moduli of the RT 92035 and RT 92036 APAO. Table IV also highlights their tensile strength and storage modulus values.

As a comparison, Table V shows some physical properties of three competitive amorphous polyalphaolefins. They range from the low softening point Polymer A to Polymer B, which shows an intermediate softening point of 260°F. The tensile strengths of these competitive polymers range from 0.8-1.8 MPa and could be considered intermediate in value between the com-

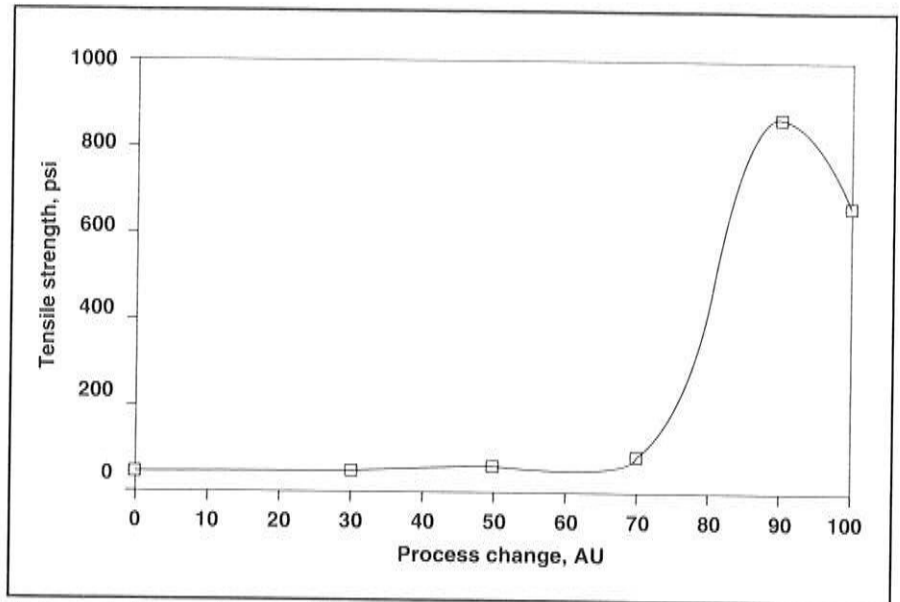


Figure 2. Dependence of tensile strength of new RT butene APAO on process changes.

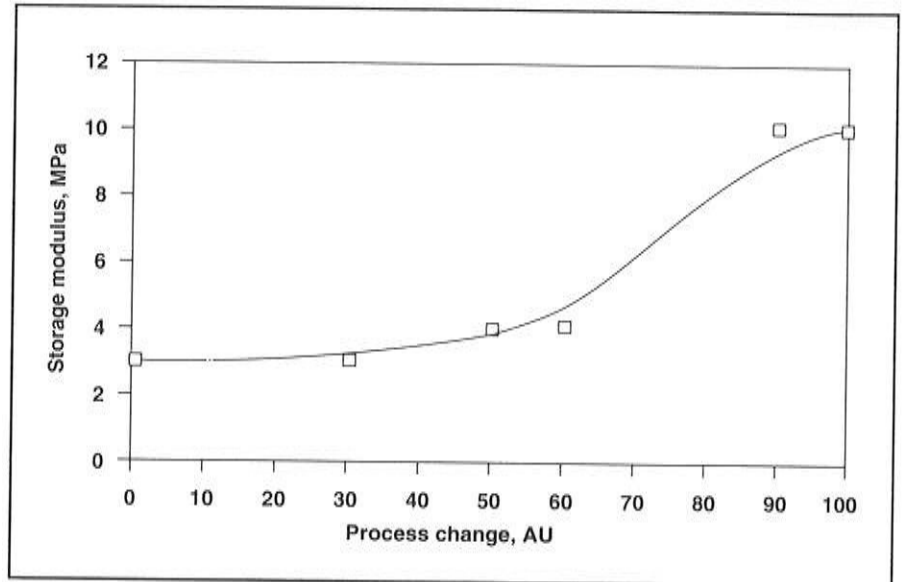


Figure 3. Dependence of the storage modulus of new RT butene APAO on process changes.

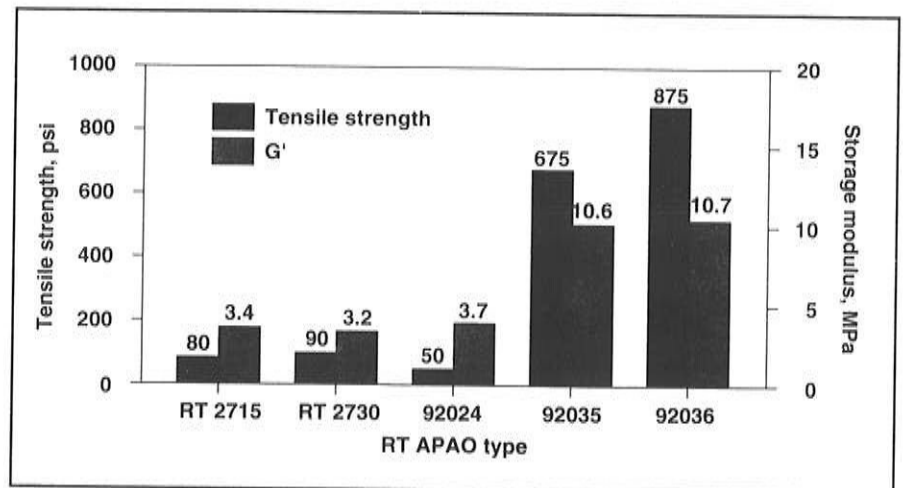


Figure 4. Tensile strength and storage modulus for commercial and developmental 1-butene RT APAO.

mercially available RT APAO and the new APAO RT 92035 and RT 92036. The same observation can be made on the values given for the storage moduli.

Conclusion

The new RT APAO will provide an expanded range of properties compared to the commercially available RT APAO. The new ethylene products exhibit higher tensile strength and an expanded range of application temperatures, although they are harder and their open times are very low. The new 1-butene RT APAO, on the other

hand, show lower softening points, but their glass transition temperatures also have decreased proportionally. More importantly, these new products show a significant increase in tensile strength and rheological properties, which will make them useful in those formulations that require a backbone APAO with high tensile strength and a sufficiently low softening point temperature.

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