

A NEW FAMILY OF HIGHER PERFORMANCE REXTAC® AMORPHOUS POLYALPHAOLEFINS, APAOs.

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ABSTRACT

Commercially available Rextac APAOs are a family of low molecular weight amorphous polyalphaolefins, APAOs, used in several different applications including hot melt adhesives and sealants. These on-purpose products are reactor-synthesized using proprietary technology, and have a range of tightly controlled properties.

The traditional envelope of physical properties and performance of Rextac is expanded by the addition of a new family of higher molecular weight, higher crystallinity polyolefins that not only show controllable higher melt viscosities and temperature resistance, but also higher tensile strength and peel adhesion values to selected substrates.

INTRODUCTION

In a hot melt adhesive in which the major component is the thermoplastic polymer, it is important that the polymer exhibit such characteristics as a range of tightly controlled Brookfield® melt viscosities (MVs), needle penetrations (NPs) and ring & ball softening points (RBSPs), controllable and predictable open time (OT), low temperature flexibility, adhesion to a variety of substrates and compatibility with a variety of tackifiers and waxes.

APAOs with tightly controlled product specifications are obtained by using a polymer manufacturing process that allows the production of a variety of these amorphous polyalphaolefins with well defined physical properties.

There are three distinctive types of on-purpose, reactor made APAOs:

- a.- homopolymers of propylene,
- b.- copolymers of propylene and ethylene and
- c.- copolymers of propylene and 1-butene.

The polymers exhibit a broad range of melt viscosities, needle penetrations, ring and ball softening points, and open times, all closely reproducible. These amorphous polyalphaolefins are synthesized by a catalyst system based on a Ziegler-Natta supported pro-catalyst and an alkyl aluminum co-catalyst. The polymerization process produces a predominantly atactic polymer.

The versatility of an on-purpose polymerization process is such that by varying process conditions like the comonomer concentration in the reactor, it is possible to obtain products that have a range of composition dependent properties [1]. For example, increasing the ethylene content in APAO results in products with increasing values in the needle penetration and lower ring and ball softening points, i.e., the APAOs become softer and less heat resistant.

In other words, proper design of the process of synthesizing the amorphous polyolefin, i.e., choice of catalyst system, of comonomer(s) and of polymerization reaction conditions, results in products that have well defined product physical and mechanical properties such as melt viscosity, softening point, needle penetration, low temperature flexibility, open time and tensile modulus.

EXPERIMENTAL

The polymers herein discussed were made using a proprietary technology and are characterized following standard test methods set forth by the American Society for Testing and Materials (ASTM) that are widely used in the hot melt adhesives industry. These test methods are:

- Melt viscosity by ASTM D-3236, measures a liquid or molten polymers internal friction-its resistance to flow. It is a most distinctive property because it determines the degree of wetting or penetration into a substrate by the molten polymer. It is a function of the polymer's molecular weight and it is reported in millipascal x sec (abbrev. mPa.s), using a Brookfield Thermosel RVT Viscometer, at a temperature of 190°C.

- Needle penetration by ASTM D-1321, measures the depth to which a weighted needle penetrates the polymer and is often used as a simple measure of softness, reported in dmm.

- Ring and ball softening point by ASTM E-28 measures the precise temperature at which a disc of polymer sample, submerged in a glycerine bath and

heated at a heating rate of 5.5°C (10°F)/min., becomes soft enough to allow a test object, a steel ball, to drop thru it. The softening point of a polymer, reported in °C (°F) is used as an indication of the polymer's heat resistance.

- Open Time by a Rexene modified ASTM D-4497 method, measures the time, in seconds, between application of a thin film of the molten polymer and the time just prior to the polymer film losing its wetting ability because of solidification [2].

Other test methods measure the polymer's heat of fusion and melting point (ASTM D-3417), glass transition temperature (ASTM D-3418) and tensile properties (ASTM D-638). The heat of fusion, in Joules/gram (J/g), determined by differential scanning calorimetry, DSC, provides a simple method for determining a polymer's degree of crystallinity.

RESULTS AND DISCUSSION

The properties and characteristics of the lower melt viscosity APAOs has been discussed before (1, 3). Their use in applications demanding high melt strength has been limited basically due to their lower molecular weight.

To address these material limitations, we have created a new generation of higher molecular weight APAOs, with melt viscosity values that are highly controllable and that range between 10,000 on up and, but not limited to, 200,000 mPa.s.

These APAOs, made using a proprietary process, show improved mechanical properties when compared with their lower melt viscosity analogs, APAOs with melt viscosities in the 400 to 8500 mPa.s. In addition, these high melt viscosity polymers also show a broad range of ring and ball softening points, needle penetrations, and open times.

We have produced several different types of high melt viscosity APAOs, of varying composition, which show a broad range of physical and mechanical properties. The E- Series polymers are medium ethylene/propylene copolymers, the BM- Series are medium 1-butene/propylene copolymers and the BH-Series are high 1-butene/propylene copolymers.

E-Series APAOs

Table 1 shows the range of melt viscosities

obtainable with these new APAOs. Included for comparative purposes is one of our commercially available products.

As the molecular weight of these polymers increases so does their heat of fusion (crystallinity), which increases from less than 5 J/g for the standard copolymer up to about 20 J/g for E-4. It then drops somewhat for E-5. This drop can be explained by both a compositional effect and by the fact that the determination of the heat of fusion of a polymer by DSC is time dependent (kinetic) and under the ASTM testing conditions, it appears that not enough time is given for the longer polymer chains to crystallize fully.

TABLE 1. Melt viscosity for ethylene/propylene APAOs.

Type	MV, mPa.s
Standard	8,500
E-1	21,000
E-2	51,000
E-3	81,000
E-4	165,000
E-5	205,000

Several properties are affected by both, the increases in molecular weight and crystallinity. For example, Figure 1 shows how as the MV of the ethylene copolymers increases from 8500 mPa.s to 205,000 mPa.s, the ring and ball softening point values increase from 141°C to 158°C.

Likewise, both the needle penetration as well as the open time drop, from about 21 dmm to 10 dmm and from 20 seconds to 0 seconds, respectively, as seen in figure 2.

A characteristic of these amorphous polymers is their low glass transition temperature. Glass transition temperature, T_g , can be described as the temperature below which there is a virtual cessation of local molecular motion, or alternatively, that temperature below which the polymer is glassy and above which it is rubbery [4]. This is an important

property when considering an application in which the polymer is part of a hot melt adhesive formulation to be used at low temperatures.

Glass transition temperatures are dependent on composition as well as, though to a lesser extent, on the molecular weight of the polymer. Simply put, the glass transition temperature is dependent on the free volume which is a function on the number of free chain ends. The shorter the molecules (lower molecular weight) the larger the number of chain ends (more free volume) and therefore polymers of lower melt viscosity show lower glass transition temperatures than their higher melt viscosity analogs.

For these new copolymers, the glass transition temperature increases from about -29°C for the standard APAO to about -20°C for APAOs E-1, E-2 and E-3 (with viscosities of up to 100,000 mPa.s). E-4 has a Tg of -19°C while the high melt viscosity E-5 has a Tg of -18°C.

It is important to keep in mind that RBSP and glass transition temperature define the temperature range where the APAO can be used without softening or becoming brittle.

One of the most informative mechanical experiments for any material is the determination of its stress-strain curve in tension, typically measured using a tensile tester. This is usually done by measuring continuously the force developed as the sample is elongated at a constant rate of extension. The load vs. elongation curve is converted to a stress-strain curve by dividing the load by the original cross-sectional area of the narrow region of the tensile bar (A_0) and dividing the elongation values by the original gage length (l_0). Since A_0 and l_0 are constants, the stress-strain curve has the same shape as the load-elongation curve [5].

The percent strain at break is taken at the highest elongation point (in displacement) in the load-displacement curve. Tensile modulus is calculated from the initial slope of the stress-strain curve. The steeper the slope, the higher the modulus value and the stiffer the APAO.

The modulus of a polymer is related to its structure (its intermolecular bonding), which determines its ability to crystallize, and to a lesser extent, to the polymer's molecular weight. Thus those polymers that possess the strongest intermolecular bonds and

the stiffest chains tend to have the highest moduli. Also, as chain length increases, the molecules become more entangled and these entanglements act as temporary crosslinks when they are stressed, enhancing the tensile modulus.

Figure 3 shows the tensile modulus and tensile strain at break values for the new ethylene/propylene copolymers. As seen, both the tensile moduli as well as the strain at break tend to increase with increased molecular weight (and crystallinity). As these polymers do not have a yield point, the stress-strain curve is shaped like a dome, with the zenith reported as the tensile strength.

It is apparent that both, increasing crystallinity and molecular weight, yields ethylene/propylene APAOs with significantly improved physical properties.

BM-Series APAOs

Table 2 shows the range of melt viscosities available with these new 1-butene/propylene APAOs which also come in a broad range of ring and ball softening point and open time values.

Table 2. Melt viscosities for medium 1-butene/propylene APAOs.

Type	MV, mPa.s
Standard	8000
BM-1	16,000
BM-2	28,500
BM-3	70,000
BM-4	145,000

Figure 4 shows how as the MV of the ethylene copolymers increases from about 8000 mPa.s to 145,000 mPa.s, the ring and ball softening point values increase from about 107°C to 158°C.

These materials are of lower crystallinity than the ethylene/propylene copolymers. The standard has a heat of fusion of less than 2 J/g, as does BM-1, while BM-2, BM-3 and BM-4 have heats of fusion of about 4.3 J/g, 6.3 J/g and 8 J/g, respectively. The increase in crystallinity results in APAOs with

decreasing values in needle penetration, from 25 dmm for the standard or 32 dmm for BM-1, to 15 dmm for BM-4, as well as open time values, from at least 240 seconds for the standard to 20 seconds for BM-4, as evidenced in figure 5.

For these medium 1-butene/propylene copolymers, the glass transition temperature increases from about -23°C for the standard APAO to about -19°C, -18°C, and -17°C for APAOs BM-1, BM-2 and BM-3, respectively. For the high melt viscosity BM-4, the T_g is -16°C.

Figure 6 shows the tensile modulus and tensile strain at break values for the new medium 1-butene/propylene copolymers. Both the tensile moduli as well as the strain at break tend to increase with increasing molecular weight, but BM-3 and BM-4 do not break at the tensile instrument's maximum elongation.

BH-Series APAOs

Table 3 shows the new high 1-butene/propylene APAOs, and their corresponding melt viscosities, again compared with one of our commercially available APAOs.

Table 3. Melt viscosities for high 1-butene/propylene APAOs.

Type	MV, mPa.s
Standard	3750
BH-1	11,100
BH-2	22,500
BH-3	37,500
BH-4	53,500
BH-5	103,000

In these new high 1-butene APAOs, as their melt viscosity increases, so does the RBSP. Figure 7 shows that the lowest MV APAO, BH-1, has a low RBSP value of 113°C (235°F), but as the molecular weight increases, so does the RBSP, and consequently BH-5, with a MV of 103,000 mPa.s, has a RBSP of 157°C (315°F).

These hard products, with low NP values, have high tensile modulus and elongation values, as seen in figure 8, which makes them very stiff and also very tough. The tensile strains at break for these polymers quickly reach a no break point. Moreover, the stress-strain curve shows that all these blends have a yield point. This type of behavior is typical of hard, tough materials that show high modulus, high elongation and high stress at break or no break. The tensile stress values at maximum elongation are higher than the tensile stresses at yield which means that these materials show strain-hardening effects.

The heats of fusion of these APAOs increases from less than 2 J/g for the standard, to 9 J/g, 13 J/g, 18 J/g, 21 J/g and 23 J/g for BH-1 to BH-5, respectively and although increasing crystallinity values shorten open times, even the highest melt viscosity, more crystalline polymer, BH-5, has a sizable open time of 40 seconds, as seen in figure 9.

For the new APAOs presented herein, the effect of the molecular weight on properties such as NP, RBSP and OT is pronounced, and it can be explained by the increase in crystallinity that occurs with increasing melt viscosity. This seems to indicate that the APAO crystalline polyolefin domains are made up of chains that contain crystallizable sequences that can serve as tie points for the non-crystalline sequences which contribute to the amorphous phase. The higher the crystallinity, the larger the number of tie-points. These tie points can indeed provide physical crosslinks during tensile deformation, just like the glassy domains in a styrene block copolymer. Collette and co-workers [6] have used this theory to explain a similar phenomenon in elastomeric polypropylene. Another factor contributing to the improvement in tensile properties is the chain entanglement caused by the longer polymer chains.

CONCLUSIONS

The new APAOs expand the range of melt viscosities available. We have found that as the molecular weight of the APAOs increase they become stiffer with improved tensile properties and higher elongation values.

We have shown that the mechanical properties of these APAOs are determined by their composition, crystallinity and molecular weight. The high 1-butene/propylene products are hard, with low NP

values, high tensile modulus, have excellent cohesive strength and a high elongation at break. The lower crystallinity, more amorphous grades, have good flexibility but have low cohesive strength and therefore low elongation at break values.

Although the MV as well as the crystallinity increases, the products show a range of closely controlled properties such as RBSP, OT, and melt viscosity. These products should also have exceptional holding power and shear adhesion failure temperature values, as well as good "green strength," which should make them highly desirable to be used in hot melt adhesive applications. Further lab work is in progress and the results will be published in future publications.

REFERENCES

- 1) B.J. Pellon and A. Sustic, 1991 TAPPI Hot Melt Symposium Notes, p. 193.
- 2) C. Cagle and H. Lee, Handbook of Adhesive Bonding, McGraw-Hill (1973).
- 3) B.J. Pellon and A. Sustic, J. Adh. Seal. Council, 20(2), 41 (1991).
- 4) D.W. Van Krevelen, Properties of Polymers, Elsevier, Chapter 6, 1976.
- 5) G.R. Moore and D.E. Kline, Properties and Processing of Polymers for Engineers, Prentice-Hall, Inc., Chapter 12, 1984.
- 6) J. W. Collette and coworkers, Macromolecules, 22, 3851 (1989).

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FIGURE 1. Melt Viscosities and Ring and Ball Softening Points for High Melt Viscosity Ethylene/Propylene APAOs.

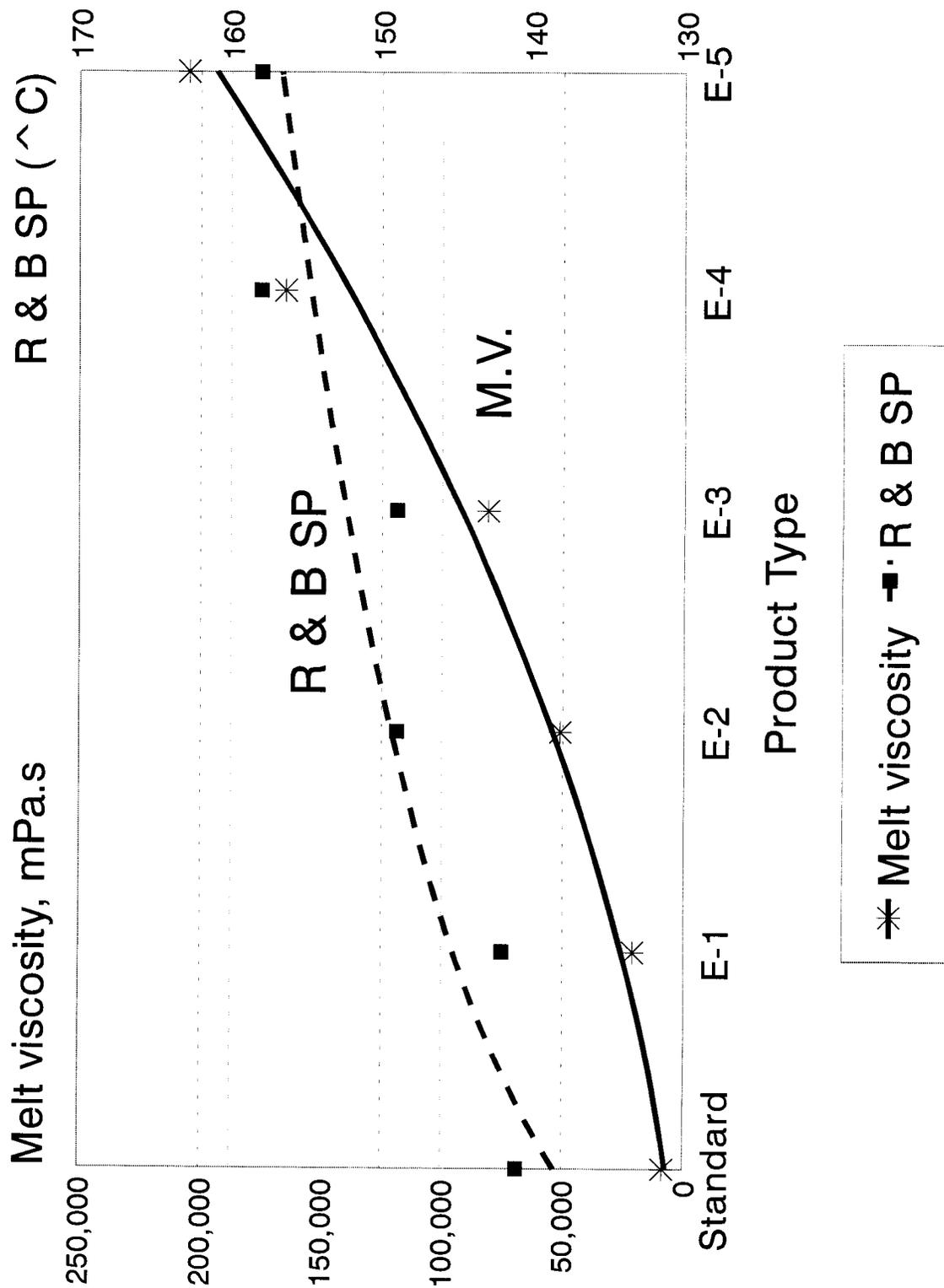


FIGURE 2. Open Times and Needle Penetrations for High Melt Viscosity Ethylene/Propylene APAOs.

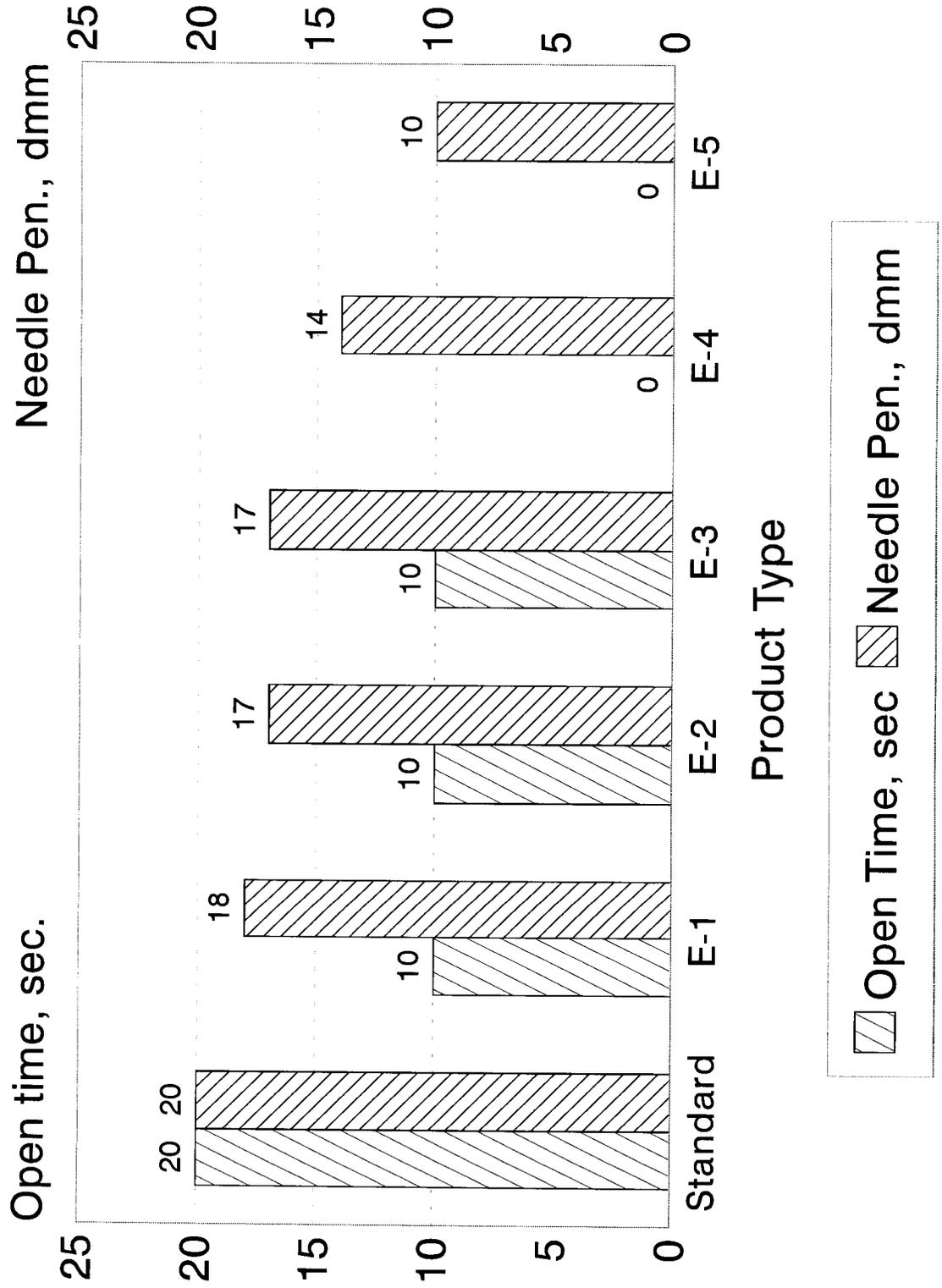


FIGURE 3. Tensile Moduli and Tensile Strain at Break for High Melt Viscosity Ethylene/Propylene APAOs.

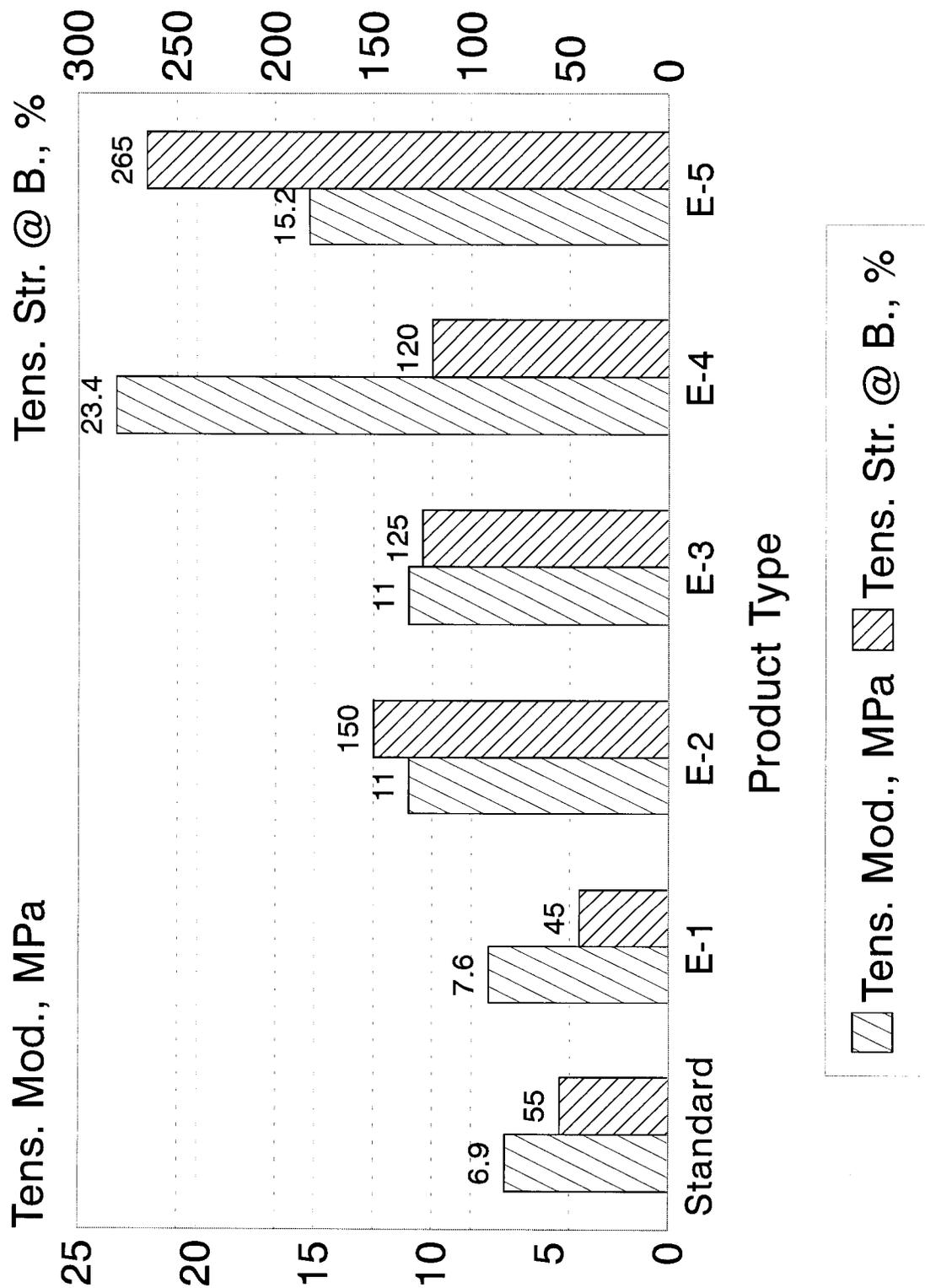


FIGURE 4. Melt Viscosities and Ring and Ball Softening Points for High Melt Viscosity Medium 1-butene/Propylene APAOs.

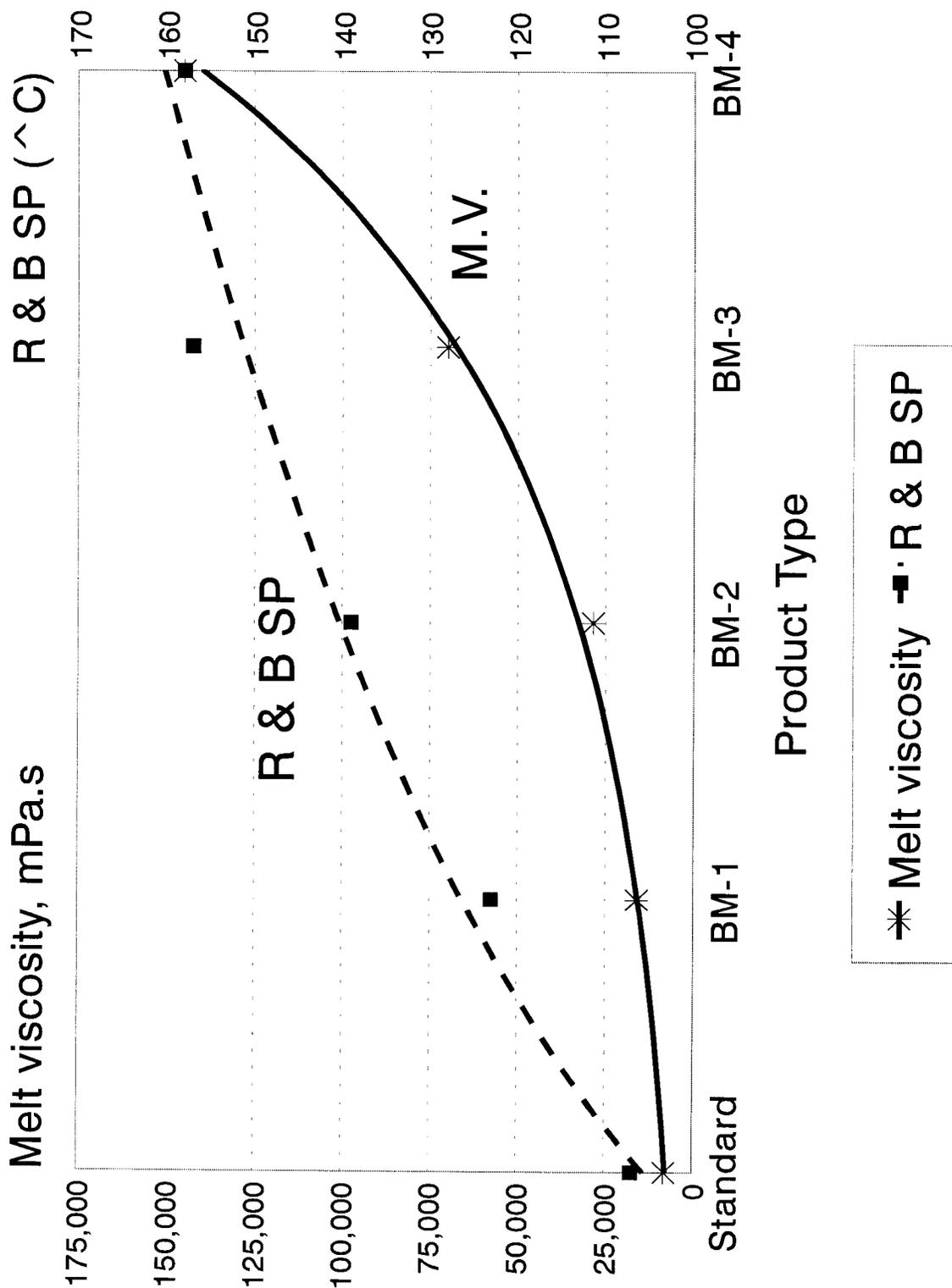


FIGURE 5. Open Times and Needle Penetrations for High Melt Viscosity Medium 1-butene/Propylene APAOs.

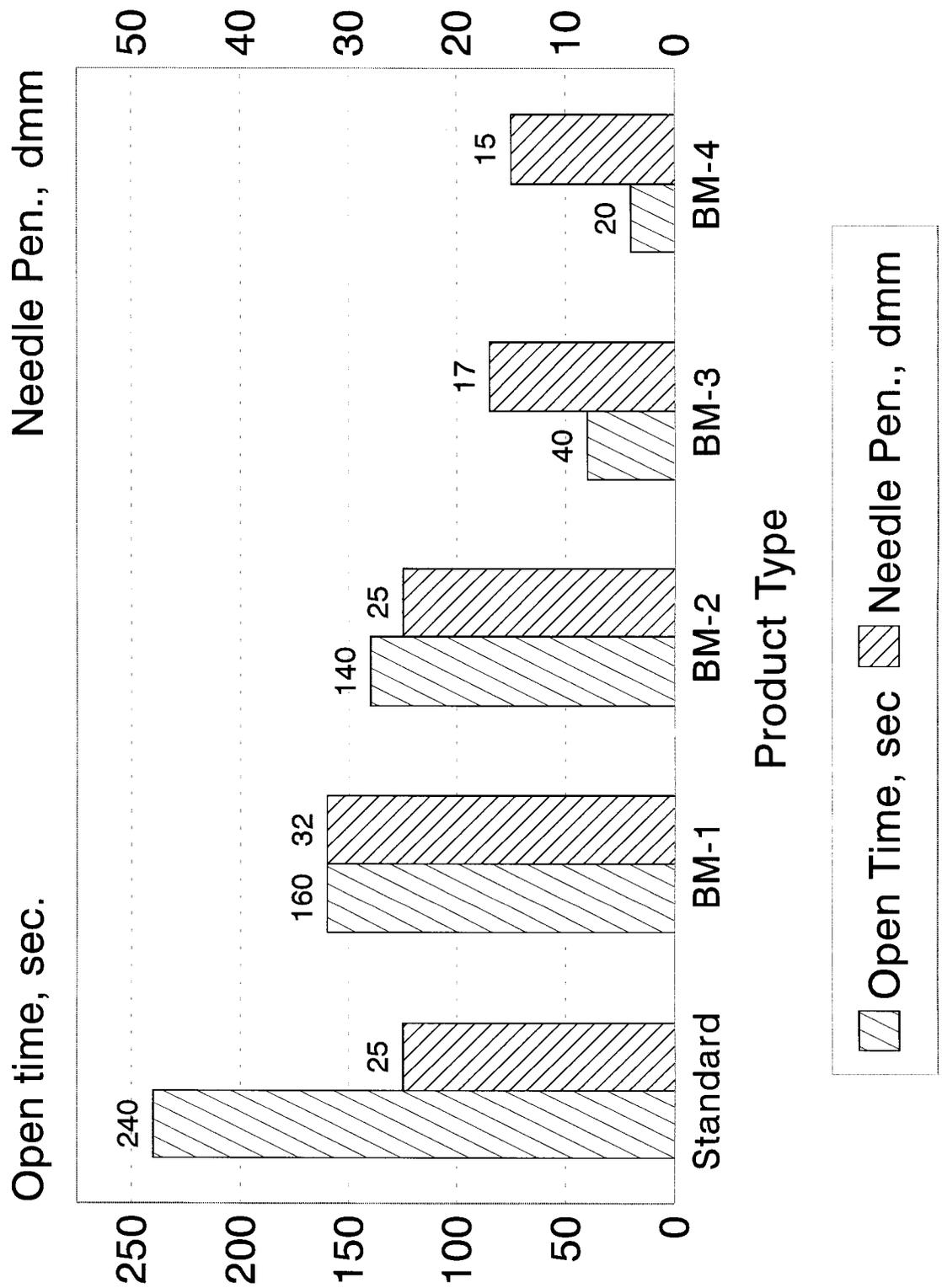


FIGURE 6. Tensile Moduli and Tensile Strain at Break for High Melt Viscosity Medium 1-butene/Propylene APAOs.

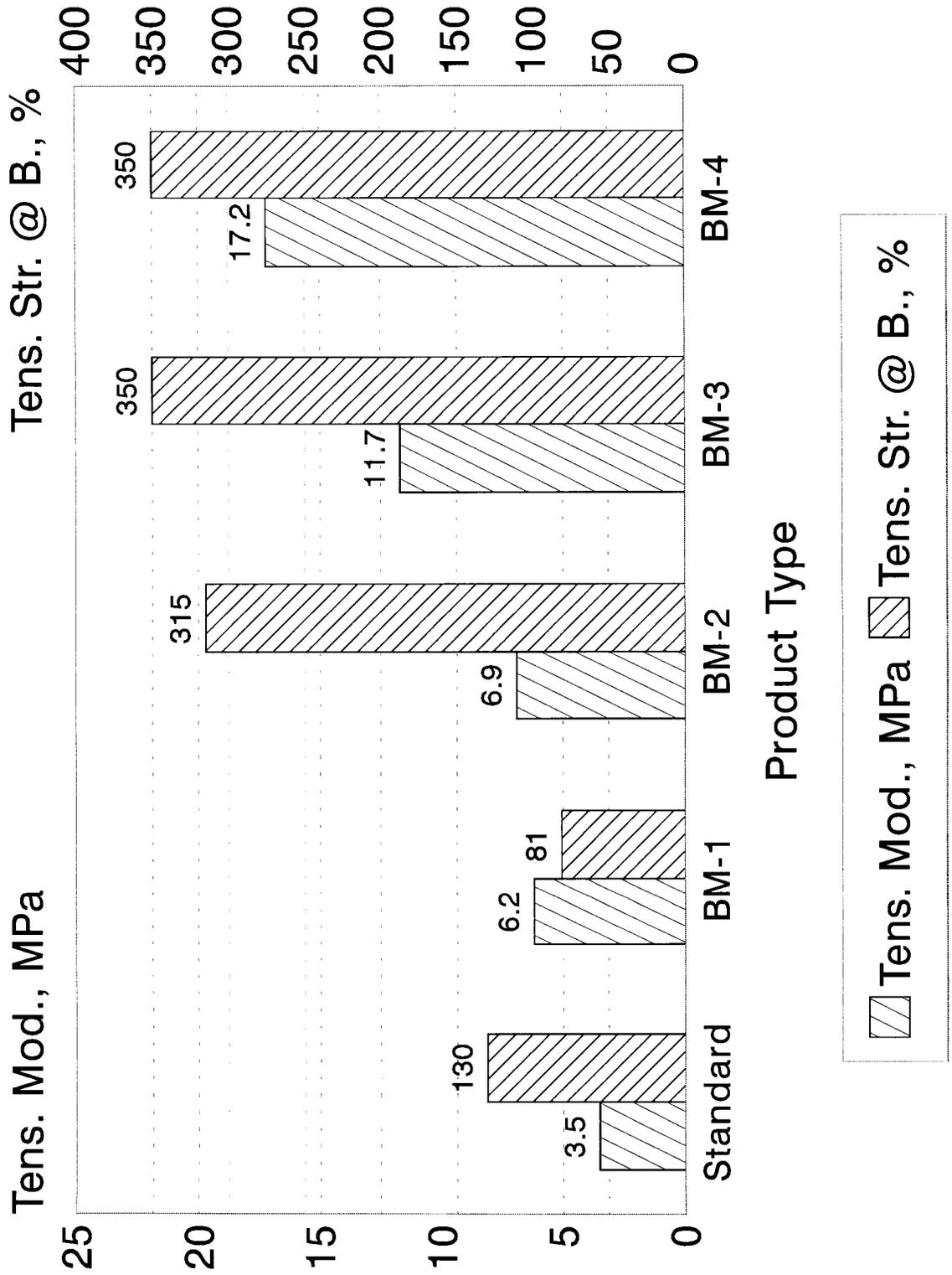


FIGURE 7. Melt Viscosities and RBSPs for High Melt Viscosity, High 1-butene/Propylene APAOs.

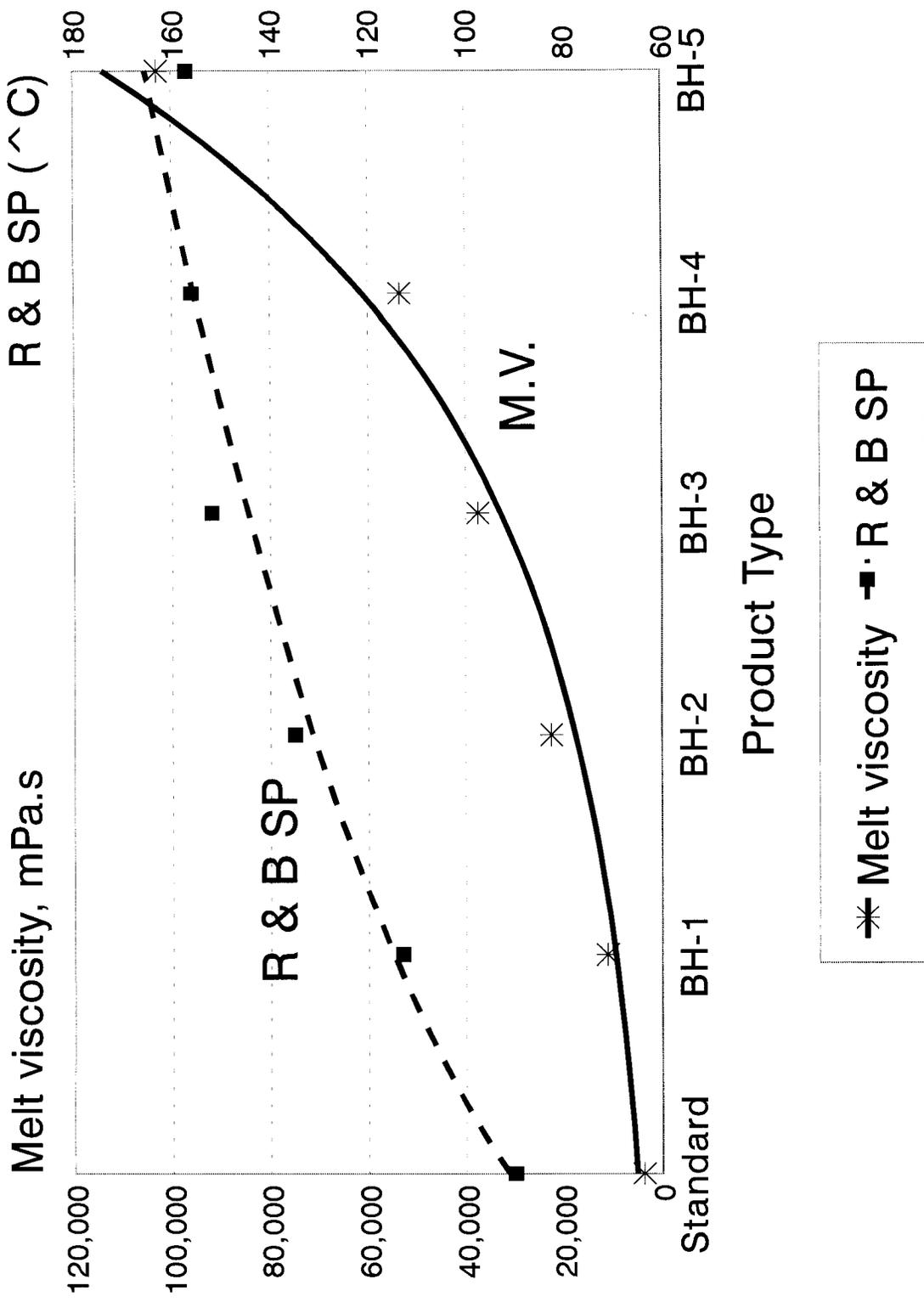


Figure 8. Melt Viscosities and Tensile Moduli for High Melt Viscosity, High 1-butene/Propylene APAOs.

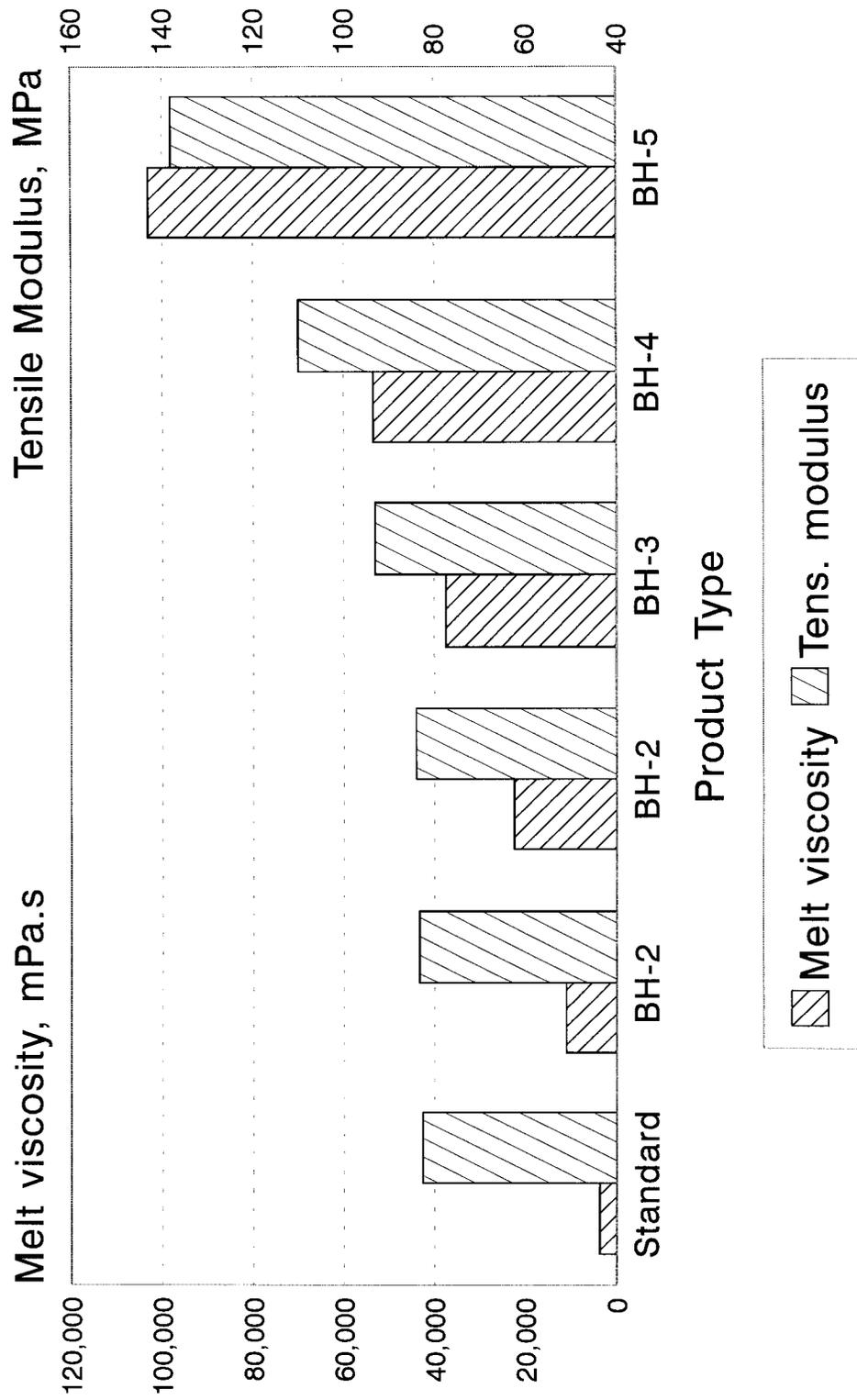


FIGURE 9. Open Times for High Melt Viscosity, High 1-butene/Propylene APAOs.

