ON-PURPOSE AMORPHOUS POLYALPHAOLEFINS USED IN HOT MELT ADHESIVES (1)

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ABSTRACT

The largest single component of a hot melt adhesive (HMA) or sealant formulation is the polymer. On-purpose amorphous polyalphaolefins (APAO), made by direct reactor synthesis, are being increasingly used today in those two areas. REXTAC® (RT) APAO are tailored co-polymers of ethylene, propylene or 1-butene and exhibit a wide range of closely reproducible physical properties such as melt viscosity, needle penetration, softening point, surface tackiness and open times.

This paper will give an in-depth description of the development and properties, including some applications, of these novel on-purpose APAO. It will also show how blending of two or more RT APAO can give products with final properties that meet specific requirements of, for instance, needle penetration, while affecting little other properties such as softening point. Finally, it will present some brief characterization data to show the versatility of these polymers in some general HMA formulations incorporating such components as tackifiers, waxes or other modifiers.

INTRODUCTION

The use of hot melt adhesives as substitutes or replacements for solvent-based adhesives in certain applications has been increasingly favored because of environmental concerns caused by the emission of VOC's and the well being of workers in the workplace (2) and also because of faster setting times. There are several different types of HMA ranging from, in order of quantities used annually, the ethylene-vinyl acetate based HMAs, followed by low molecular weight PE, amorphous polyolefin and elastomer-based HMA to the higher priced polyester and polyamide based HMAs.

Amorphous polypropylene, APP, which is still used in some HMA applications, is a by-product of the synthesis of isotactic polypropylene (IPP) and because of the nature of the process which produces IPP, frequently has broad specifications for such properties as melt viscosity (MV), needle penetration (NP) and ring and ball softening point (RBSP).

The development of new catalysts which are highly active and stereospecific has meant that the proportion of atactic polymer in the polymers produced employing these catalysts are substantially reduced and therefore the polymer product generally does not require any purification to remove the atactic or low crystalline fraction. That means that APP supply from polypropylene (PP) plants using standard first generation Ziegler-Natta catalysts is decreasing as commercial plants continue to convert to high activity catalysts. Very little by-product APP is produced with the use of these new catalysts in PP manufacture.

It would be highly desirable to the HMA formulator to have an APAO polymer produced to close specifications. This has been accomplished by properly designing the process of synthesizing the amorphous polyolefin, specifically, proper choice of the catalyst system and of comonomers results in products which have well defined melt viscosity, softening point, needle penetration, embrittlement temperature and open time.

RESULTS AND DISCUSSION

APAO

The amorphous polyalphaolefins are synthesized by a specially designed catalyst system based on a Ziegler-Natta supported catalyst and an alkyl aluminum cocatalyst. The polymerization process produces a mostly atactic, amorphous polymer. These polymers exhibit low crystallinity which clearly depends on the copolymer structure.

There are three distinctive product types of on-purpose APAO produced by our reactor.

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

The homopolymers are designated as the RT 2100 series, the RT 2200 are the low ethylene copolymers, the RT 2300 are medium ethylene copolymers, the RT 2500 are high ethylene copolymers and the RT 2700 are the 1-butene copolymers. The last two digits describe the viscosity measured at 190°C (375°F) in poise, e.g., RT 2330 is a medium ethylene copolymer with a melt viscosity of 3000 cps.

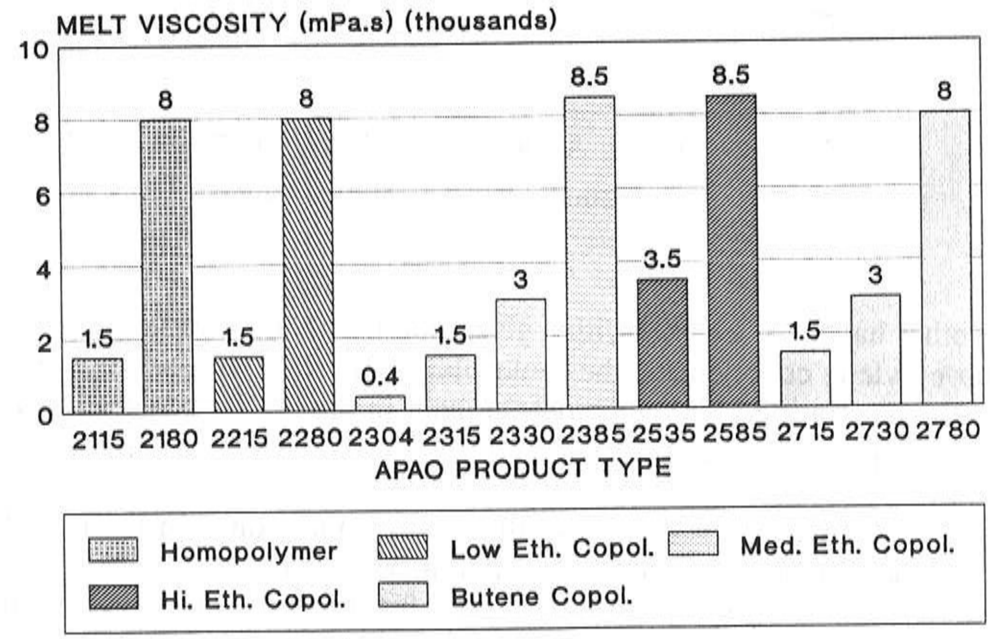
APAO PROPERTIES

Melt Viscosity

In a Hot Melt Adhesive, the melt viscosity 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. Low melt viscosity is desirable for most hot melt applications making the HMA amenable to be used at temperatures low enough to avoid distortion of thin plastic substrates. This allows it to be used in applications where controlled fiberization or spraying are employed.

Melt viscosity is determined by molecular weight which is controlled in process by the precise addition of a modifier. This allows the obtainment of products with a wide range of melt viscosities, Fig. 1. The melt viscosity is determined at 375°F (190°C) following ASTM Test Method D-3236.

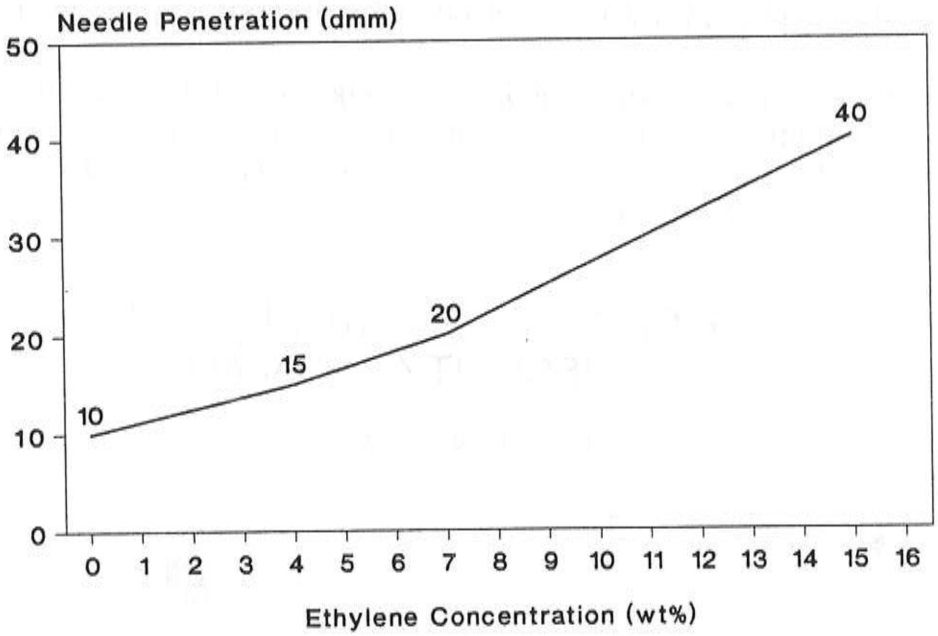
FIGURE 1. BROOKFIELD MELT VISCOSITY OF APAO



Needle Penetration

With thermoplastics and elastomers, hardness is often used as a simple measure of stiffness. The needle penetration indicates the resistance to deformation (or hardness) of the polymer. It was determined following ASTM Test Method D-1321. Varying the polymer composition such as increasing the concentration of ethylene, makes it possible to obtain products that show increasing values in the needle penetration, i.e., the APAO become softer, Fig. 2.

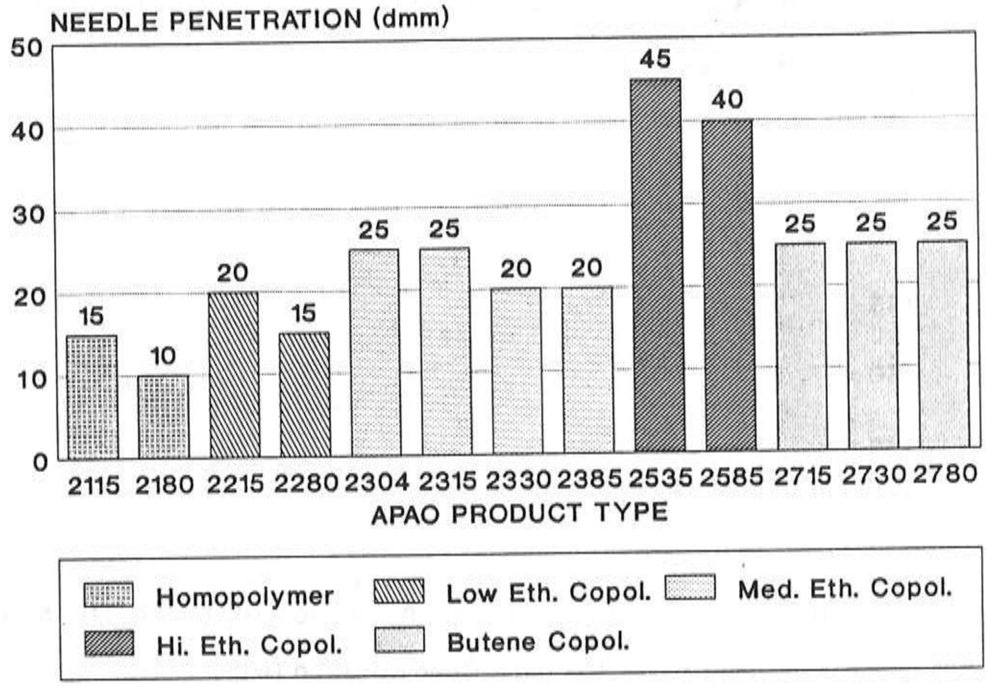
FIGURE 2. EFFECT OF ETHYLENE CONCENTRATION ON THE NEEDLE PENETRATION OF APAO



On the other hand, for a series with a given ethylene concentration, e.g. the 2300, the medium ethylene copolymers, the molecular weight has a relatively small effect on the needle penetration. The main determinant in the needle penetration values is the polymer composition, Fig. 3.

Hardness is also determined by crystallinity. As mentioned in the Introduction, the APAO are amorphous, mostly atactic polymers. However there is some residual crystallinity as evidenced from the heats of fusion and heptane insolubilities. For instance, from the homopolymers to the high ethylene copolymers, the APAO become more amorphous with heats of fusion decreasing from 26 J/g to 8 J/g while their solubilities in boiling heptane is almost complete, particularly so in the case of the 1-butene copolymers which are completely soluble in boiling heptane. The solubility of the APAO at ambient temperature after contacting with aromatic solvents such as toluene or xylene for 24 h, ranges from about 75 % to 100 %.

FIGURE 3. NEEDLE PENETRATION OF APAO



Ring and Ball Softening Point

The softening point of a polymer is important in hot melt adhesives in that it has a major influence on the heat resistance, application temperature and open time. As is the case for the needle penetration, the softening point is primordially determined by the copolymer composition. In particular for the ethylene copolymers, increasing the comonomer concentration decreases the softening point as evidenced in Fig. 4; the molecular weight has little effect on the softening point of the copolymers. Fig. 5 shows the softening point of all the APAO. It is evident that as the comonomer content of the copolymers increases, the softening point decreases with the lowest values being shown by the butene copolymers. The softening point was determined following ASTM Test Method E-28.

FIGURE 4. EFFECT OF ETHYLENE CONCENTRATION ON THE SOFTENING POINT OF APAO

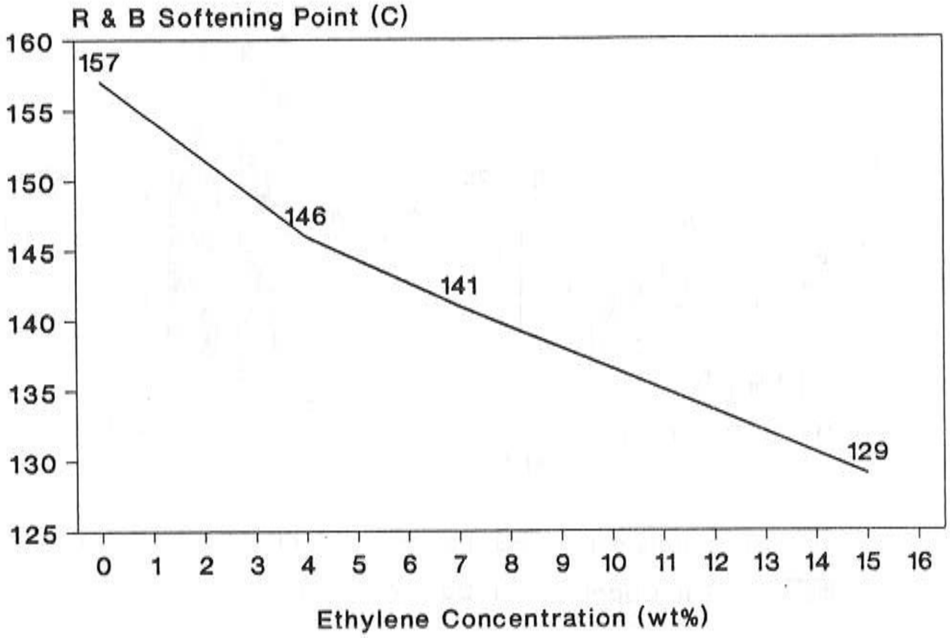
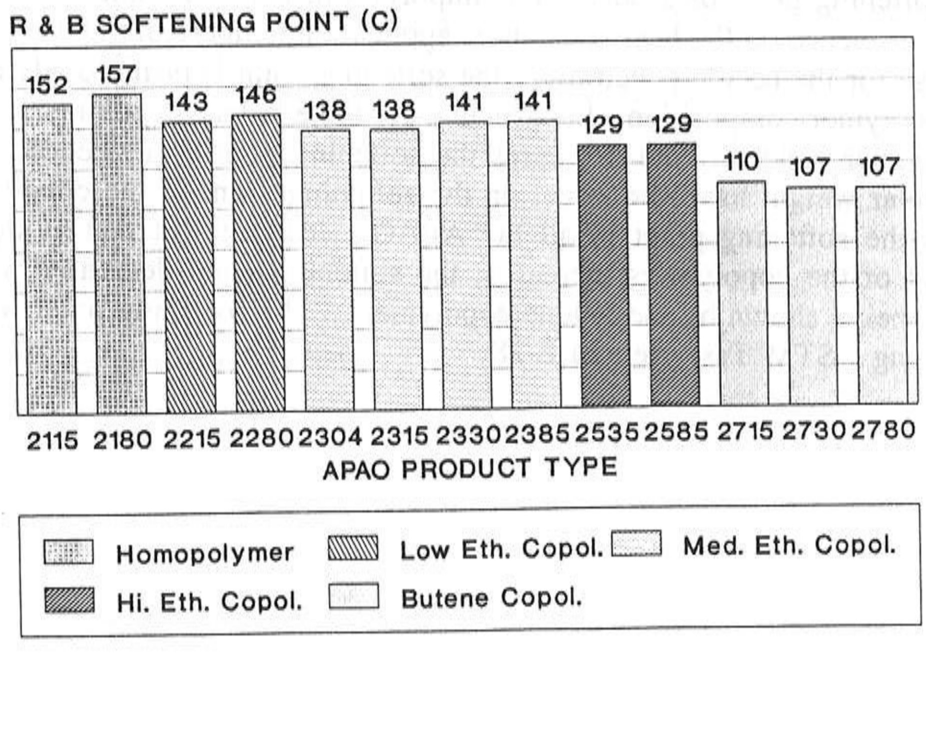


FIGURE 5. RING AND BALL SOFTENING POINT OF APAO



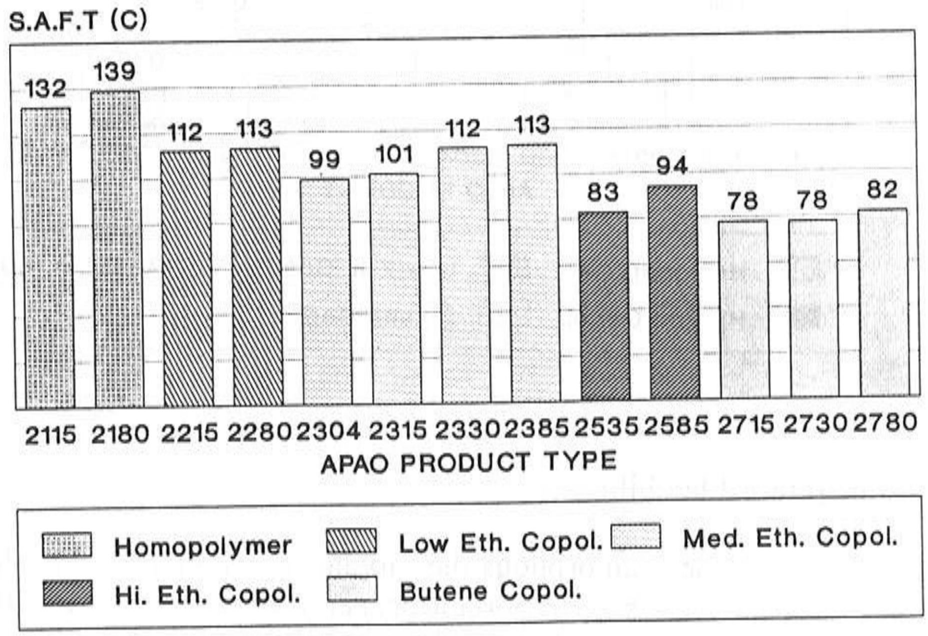
Open Time

Open time can be defined as the time between applying a hot melt adhesive and the time just prior to the hot melt's loosing its wetting ability because of solidification [3]. The open time of the polymers is controlled also by the composition. As comonomer is added, the values range from very low (< 10 sec) for the homopolymers to long (> 60 sec) for the butene copolymers.

Shear Adhesion Failure Temperature

The shear adhesion failure temperature determines the temperature at which specimens bonded with HMA delaminate under static load in shear mode. The SAFT is mainly determined by polymer composition and somewhat by molecular weight. Fig. 6 shows how the SAFT decreases as the concentration of ethylene increases in the copolymers. Looking at it from another angle, SAFT is proportional to the softening point of the copolymer; higher softening point products show a correspondingly higher SAFT.

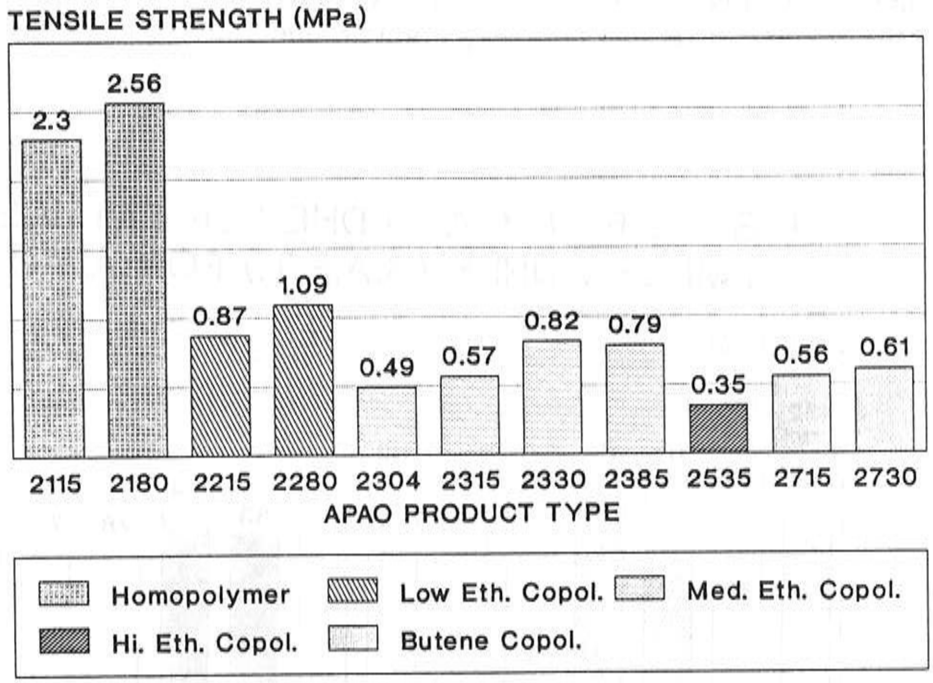
FIGURE 6. SHEAR ADHESION FAILURE TEMPERATURES (S.A.F.T.) FOR APAO



Tensile Strength

The tensile strength of a polymer is an important factor in the cohesive strength of an adhesive. Fig. 7 shows the tensile strength of the APAO with the homopolymers showing the highest values. As the ethylene content in the copolymers increases, the tensile strength decreases, very much in agreement with the increasing softness as measured by softening point and needle penetration. Within a particular series, the tensile strength increases with molecular weight, up to a certain extent. In general, with increasing molecular weight, the chain entanglements as well as the intrachain interactions increase. An apparent exception to this trend is the tensile strength values for 2330 and 2385 which are quite similar to each other (as is their SAFT). 2780 did not yield, showing an elongation > 700 %.

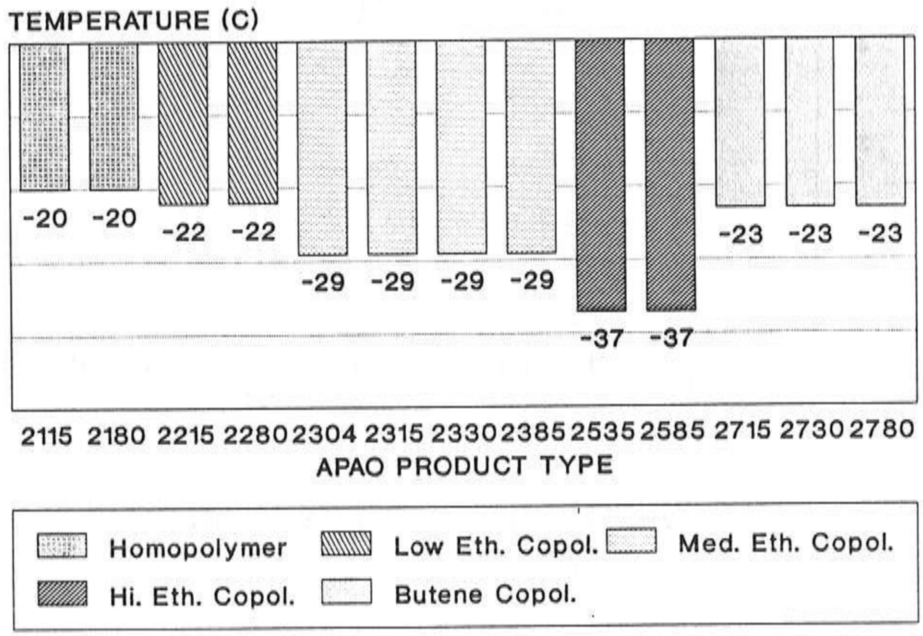
FIGURE 7. TENSILE STRENGTH OF APAO



Low Temperature Flexibility

A characteristic of these amorphous thermoplastic polymers is their low temperature flexibility (LTF). This is an important property when considering an application in which the polymer is going to be used in a HMA to be stored at low temperature, for instance, in the freezer-to-oven meal packages or in a sealant that is going to be used in a cold weather climate. The low temperature flexibility is related to the glass transition temperature (Tg) determined by DSC. Fig. 8 shows the low temperature flexibility of APAO and it is evident that the softer the APAO the lower the low temperature flexibility. As with other physical properties such as needle penetration and softening point, low temperature flexibility is constant for a constant ethylene concentration, independent of the molecular weight, but it is dependent on the copolymer composition.

FIGURE 8. LOW TEMPERATURE FLEXIBILITY/ GLASS TRANSITION TEMPERATURE FOR APAO



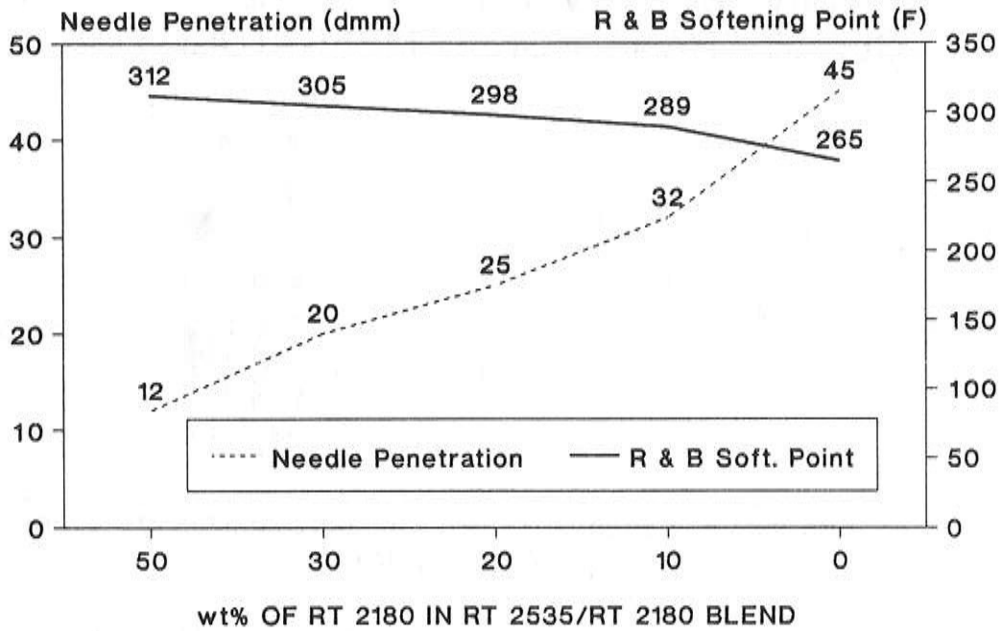
APAO BLENDS

Intra-APAO Blends

As blends between RT APAO are compatible, it is possible to obtain a blend with a melt viscosity of say, 5000 cps, by blending for example, 7 parts of RT 2535 and 3 parts of RT 2585. Other properties like the needle penetration and the softening point will remain unchanged. Blending would also be an alternative if a polymer is needed with a certain specific ethylene content, not directly available in one of the RT APAO products or if one is aiming for a needle penetration or a softening point or a tensile strength with a value not directly available in any neat polymer.

This widening of the properties can be successfully achieved because, as already noted above, the reactor-made APAO can be produced with tightly controlled properties. Fig. 9 shows the effect on the needle penetration and on the softening point of adding to a high ethylene copolymer, (RT 2535), increasing quantities of the homopolymer RT 2180. While the change in softening point is relatively small, the blend becomes appreciably harder as more RT 2180 is being added to the blend.

FIGURE 9. EFFECT OF RT 2180 CONTENT ON THE NP AND RBSP OF 2535/2180 BLEND

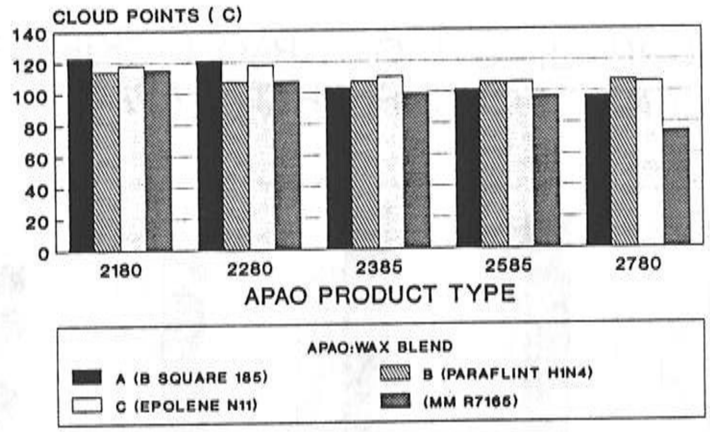


Blends with Tackifiers

Tackifiers are added to adhesive formulations to increase the adhesion of the polymer to various substrates. This is accomplished by reducing the viscosity of the hot melt which facilitates the wetting of the substrate. Table 1 shows data on compatibility of APAO with a variety of tackifiers. The compatibility, as determined by the Cloud Point (C.P.) of the blend, which is the temperature at which a clear melt of two or more components starts to cloud up as it cools from the melt to a solid, is best with tackifiers of a hydrocarbon or hydrogenated alicyclic nature while with aromatic tackifiers, the APAO show total incompatibility. With a rosin ester tackifier, the presence of the polar ester groups causes the APAO blends to show limited compatibility, requiring temperatures in excess of 160°C to show clear blends.

Notice also that, in general, the C.P. of the binary blends decreases proportionally with the softening points of the neat APAO. Fig. 10 which shows the cloud points of three different APAO/tackifier blends where the APAO used have a MV of 1500 cps. Even at ambient temperature, the blends appeared slightly cloudy.

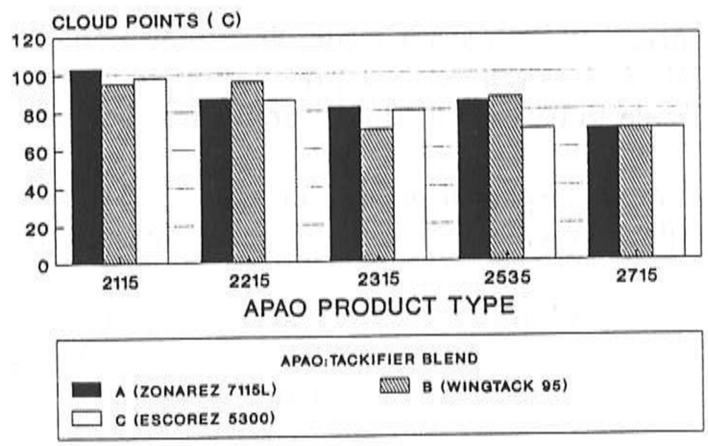
FIGURE 11. C.P. OF APAO:WAX BLENDS FOR DIFFERENT APAO PRODUCT TYPES



<u>Blends with waxes</u>

Waxes are used in HMA to reduce the viscosity and adjust the softening point and open time. Compatibility of APAO with microcrystalline as well as with Fischer-Tropsch, synthetic polyethylene, and paraffinic waxes, respectively, as shown in Table 2, is excellent at high temperatures. At high temperature, the melts are clear while at room temperature, the blends are opaque and the C.P., as was the case for the APAO/tackifier blends, is determined by the softening point of the APAO, as seen in Fig. 11 for blends of said waxes with APAO of a nearly constant MV of 8000 cps.

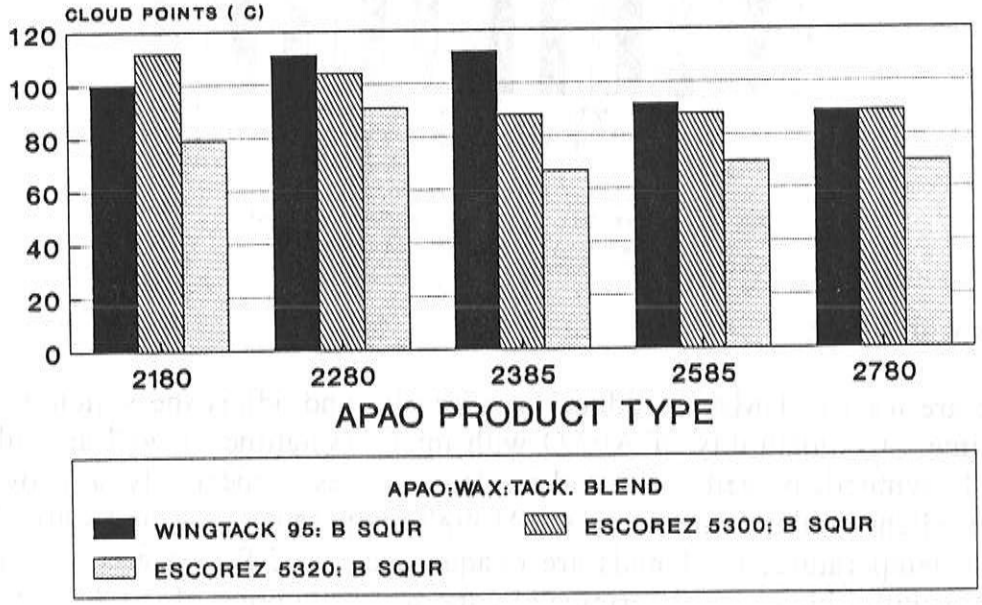
FIG. 10. CLOUD POINTS OF APAO:TACKIFIER BLENDS FOR DIFFERENT APAO PRODUCT TYPES



Blends with tackifiers and waxes

The C.P. of ternary blends of APAO:tackifier:wax are shown in Table 3. It is interesting to note that the addition of microcrystalline wax to the APAO:Escorez 5320 blend makes for a more compatible blend. From Table 2, the compatibility of APAO with the alicyclic tackifier Escorez 5320 is poor. However, on addition of the microcrystalline wax B Square 185, a highly compatible blend is obtained, as evidenced in Fig. 12.

FIGURE 12. C.P. OF APAO:TACKIFIER:WAX BLENDS FOR DIFFERENT APAO TYPES



B SQUR STANDS FOR B SQUARE 185 WAX

SUMMARY

- Because they are reactor made, the on-purpose APAO presented herein show a range of closely controlled properties which makes them highly desirable to be used in HMA formulations.

- Due to closely controlled properties it is possible, by intra-APAO blending, to widen the range of properties available at one's disposal.

- The compatibility of APAO in blends with tackifiers and waxes is directly related to their chemical affinity, APAO being mostly compatible with modifiers of an aliphatic, non-polar nature.

APPENDIX A

TEST METHODS

Cloud Point	AMS 360.22 (Exxon Test Method)
S.A.F.T.	TMHM-023 (H. B. Fuller Test Method)
Open Time	REXENE Method

APPENDIX B

LIST OF SUPPLIERS

PRODUCT	SUPPLIER	COMPOSITION
ESCOREZ 5300®	EXXON CHEMICALS	Hydrogenated cyclic tackifier (300 cps @ 350°F)
ESCOREZ 5320®	EXXON CHEMICALS	Hydrogenated cyclic tackifier (1500 cps @ 350°F)
ESCOREZ 7105®	EXXON CHEMICALS	Aromatic tackifier
ZONAREZ 7115L®	ARIZONA CHEMICAL COMPANY	Dipentene resin tackifier
ZONESTER 100®	ARIZONA CHEMICAL COMPANY	Pentaerythritol ester of tall oil rosin
WINGTACK 95®	GOODYEAR CHEMICALS	C_5 Synthetic polyterpene tackifier
PICCOTEX LC®	HERCULES	Aromatic tackifier
B SQUARE 185®	PETROLITE	Microcrystalline wax
PARAFLINT H1N4®	MOORE & MUNGER MARKETING	Fischer-Tropsch wax
EPOLENE N11®	EASTMAN CHEMICAL COMPANY	Low MW PE wax
R-7165®	MOORE & MUNGER MARKETING	Fully refined paraffin wax

REFERENCES

1. Parts of this paper were presented at the 1991 TAPPI HMA Meeting.

2. Business Research Report B149: Hot Melt Adhesives.

3. C. Cagle and H. Lee, Handbook of Adhesive Bonding, McGraw-Hill (1973).

ACKNOWLEDGMENTS

The authors wish to thank J. Newsom and P. Sparkman for their assistance in conducting some of the experiments and M. Agee for obtaining the tensile data.

TABLE 1. CLOUD POINTS OF APAO : TACKIFIER BLENDS

PRODUCT NAME	RING & BALL SP °C(°F)	C.P. BLEND A R.T. 190°C	C.P. BLEND B R.T. 190°C	C.P.BLEND C R.T. 190°C
2115	152 (305)	s.c. cl (100-105°C)	s.c. cl (95°C)	c cl (97-100°C)
2180	157 (315)	s.c. cl (95-100°C)	s.c. cl (98-103°C)	c cl (99-102°C)
2215	143 (290)	s.c. cl (85-90°C)	s.c. cl (96°C)	c cl (85-86°C)
2280	146 (295)	s.c. cl (91-93°C)	s.c. cl (94-98°C)	c cl (82-84°C)
2304	138 (280)	s.c. cl (80-82°C)	s.c. cl	c cl (79-80°C)
2315	138 (280)	s.c. cl (80-83°C)	s.c. cl	s.c. cl (79-80°C)
2330	141 (285)	s.c. cl (80-85°C)	s.c. v.s.c.	s.c. cl (72-73°C)
2385	141 (285)	s.c. cl (< 75°C)	vsc vsc	s.c. cl (75-78°C)
2535	129 (265)	s.c. cl (< 85°C)	s.c. cl (85-90°C)	v.s.c. cl (< 70°C)
2585	129 (265)	s.c. cl (< 75°C)	v.s.c. cl	c cl (< 70°C)
2715	110 (230)	s.c. cl (< 70°C)	v.s.c. cl	cl cl
2730	107 (225)	s.c. cl (< 70°C)	v.s.c. cl	cl cl
2780	107 (225)	s.c. cl (< 85°C)	s.c. cl	s.c. cl

BLEND A = APAO : ZONAREZ 7115L = 1 : 1
BLEND B = APAO : WINGTACK 95 = 1 : 1
BLEND C = APAO : ESCOREZ 5300 = 1 : 1

cl = clear
v.s.c. = very slightly cloudy
s.c = slightly cloudy
c = cloudy
o = opaque
I = incompatible, 2 phases

TABLE 1 (Cont.). CLOUD POINTS OF APAO : TACKIFIER BLENDS

PRODUCT NAME	RING & BALL SP °C (°F)	C.P. BLEND D R.T. 190°C	C.P. BLEND E R.T. 190°C	C.P.BLEND F R.T. 190°C
2115	152 (305)	I I	c c	o c
2180	157 (315)	I I	c c	o c
2215	143 (290)	I I	c s.c.	o c (187°C)
2280	146 (295)	I I	c c	o c
2304	138 (280)	I I	c v.s.c.	o c (161°C)
2315	138 (280)	I I	c s.c.	o c (172°C)
2330	141 (285)	I I	c c	o c (169°C)
2385	141 (285)	I I	c c	o c
2535	129 (265)	I I	c v.s.c.	o c (185°C)
2585	129 (265)	I I	c s.c.	o c (189°C)
2715	110 (230)	I I	c c	o c
2730	107 (225)	I I	c c	o c
2780	107 (225)	I I	c c	o c

BLEND D = APAO : PICCOTEX LC = 1 : 1
BLEND E = APAO : ESCOREZ 5320 = 1 : 1
BLEND F = APAO : ZONESTER 100 = 1 : 1

T A B L E 2. CLOUD POINTS OF APAO : WAX BLENDS

PRODUCT NAME	C.P.BLEND A R.T. 190°C	C.P. BLEND B R.T. 190°C	C.P. BLEND C R.T. 190°C	C.P.BLEND D R.T. 190°C
2115	o cl (133°C)	o cl (111°C)	o cl (116°C)	o cl (113°C)
2180	o cl (123°C)	o cl (114°C)	o cl (118°C)	o cl (115°C)
2215	o cl (108°C)	o cl (112°C)	o cl (119°C)	o cl (106°C)
2280	o cl (121°C)	o cl (108°C)	o cl (118°C)	o cl (107°C)
2304	o cl (108°C)	o cl (104°C)	o cl (112°C)	o cl (104°C)
2315	o cl (104°C)	o cl (106°C)	o cl (105°C)	o cl (95°C)
2330	o cl (105°C)	o cl (107°C)	o cl (116°C)	o cl (103°C)
2385	o cl (103°C)	o cl (107°C)	o cl (110°C)	o cl (99°C)
2535	o cl (99°C)	o cl (106°C)	o cl (109°C)	o cl (104°C)
2585	o cl (101°C)	o cl (106°C)	o v.s.c. (106°C)	o cl (97°C)
2715	o cl (100°C)	o cl (106°C)	o v.s.c. (104°C)	o cl (81°C)
2730	o cl (99°C)	o cl (105°C)	o v.s.c. (106°C)	o cl (78°C)
2780	o cl (97°C)	o cl (106°C)	o v.s.c. (106°C)	o cl (74°C)

BLEND A = APAO : B SQUARE 185 = 1 : 1
BLEND B = APAO : PARAFLINT H1N4 = 1 : 1
BLEND C = APAO : EPOLENE N11 = 1 : 1
BLEND D = APAO : R7165 = 1 : 1

TABLE 3. CLOUD POINTS OF APAO : TACKIFIER : WAX BLENDS

PRODUCT NAME	C.P.BLEND A R.T. 190°C	C.P. BLEND B R.T. 190°C	C.P. BLEND C R.T. 190°C	C.P.BLEND D R.T. 190°C
2115	o cl (114°C)	o cl (102°C)	o o	s.c. cl (90°C)
2180	o cl (100°C)	o cl (112°C)	o o	v.s.c. cl (79°C)
2215	o cl (101°C)	o cl (117°C)	o o	s.c. cl (81°C)
2280	o cl (111°C)	o cl (104°C)	o o	v.s.c. cl (91°C)
2304	o cl (110°C)	o cl (111°C)	o o	s.c. cl (69°C)
2315	o cl (109°C)	o cl (110°C)	o o	s.c. cl (77°C)
2330	o cl (99°C)	o cl (107°C)	o o	v.s.c. cl (73°C)
2385	o cl (112°C)	o cl (88°C)	o o	v.s.c. cl (67°C)
2535	o cl (98°C)	o cl (90°C)	o o	v.s.c. cl (53°C)
2585	o cl (92°C)	o cl (88°C)	o o	v.s.c. cl
2715	o cl (92°C)	o cl (86°C)	o o	v.s.c. cl
2730	o cl (19°C)	o cl (87°C)	o o	v.s.c. cl
2780	o cl (89°C)	o cl (89°C)	o o	v.s.c. cl

BLEND A = APAO : WINGTACK 95 : B SQUARE 185 = 1 : 1 : 1
BLEND B = APAO : ESCOREZ 5300 : B SQUARE 185 = 1 : 1 : 1
BLEND C = APAO : ESCOREZ 7105 : B SQUARE 185 = 1 : 1 : 1
BLEND D = APAO : ESCOREZ 5320 : B SQUARE 185 = 1 : 1 : 1