NOVEL AMORPHOUS POLYALPHAOLEFINS (APAO) IN HOT MELT ADHESIVE FORMULATIONS

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ABSTRACT

On-purpose amorphous polyalphaolefins (APAO), made by direct reactor synthesis, are being used in increasing amounts in hot melt adhesives (HMA). The products are tailored copolymers of ethylene, propylene or 1-butene and exhibit a range of melt viscosities, needle penetrations and softening points, surface tackiness and open times; all closely reproducible.

This paper describes briefly the development of these novel on-purpose APAOs. It will show data on physical and mechanical properties as well as present characterization data which intends to show the versatility of these compounds in some general HMA formulations.

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 (1) 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 rubber-based to the higher priced polyester and polyamide based HMAs.

The amorphous polyolefin based hot melts are widely used in such areas as packaging, non-wovens and product assembly, and are highly suitable for adhering paper or foil to a variety of substrates. In 1988 about 121 MM lbs of APP and APAO were consumed in HMA. They accounted for 15 percent of total raw materials used in HMA (1).

In a HMA 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 (MV), needle penetrations (NP) and ring & ball softening points (RBSP), controllable and predictable open time (OT), low temperature flexibility, adhesion to a variety of substrates and compatibility with a variety of tackifiers and waxes. Amorphous polypropylene, APP, which is still used in some HMA applications, is a by-product of the synthesis of isotactic polypropylene (IPP) and frequently has broader specifications for those properties mentioned above. Moreover, APP supply from polypropylene (PP) plants using standard first generation Ziegler-Natta catalysts will decrease 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 can be accomplished by modifying the process of synthesizing the amorphous polyolefin, specifically, designing the catalyst system which allows one to obtain a variety of polymers with well defined physical properties. This paper shows we have done this.

RESULTS AND DISCUSSION

APAO

The amorphous polyalphaolefins are synthesized by a catalyst system based on a Ziegler-Natta supported catalyst and an alkyl aluminum cocatalyst. The polymerization process produces a mostly atactic polymer. A polymer such as polypropylene is considered atactic when the placement of the methyl substituents in the hydrocarbon backbone is random as seen from the top of an imaginary plane that rests longitudinal to the polymer chain. As these APAO show little crystallinity (as determined from the DSC heats of fusion) and are almost completely soluble in boiling heptane and cold xylene, they are considered amorphous. Amorphous character is also introduced by copolymerization with such monomers as ethylene.

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.

Adjusting the reaction conditions such as increasing the concentration of ethylene in the copolymer, makes it possible to obtain products that at a nearly constant M.V., show an increasing degree of softness as evidenced by the increase in the NP, Fig. 1a, and the decrease in the RBSP, Fig. 1b. The open time (OT) of the polymers is controlled also as ethylene is added as a comonomer with values ranging from very low (<10 sec) to long (> 60 sec).

Incorporation of 1-butene gives copolymer products with long OT and low softening points of around 107°C (225°F). In general, for a series of copolymers, the molecular weight has little influence on the NP and the RBSP.

As mentioned above, these polymers exhibit low crystallinities which clearly depend on the copolymer structure. For instance, going from the homopolymers to the high ethylene copolymers, the APAO become more amorphous with heats of fusion ranging from 26 J/g to 8 J/g while their solubility in refluxing heptane ranges from 98 to 100 wt%. The same is true for the 1-butene copolymers. As a comparison, the DSC crystallinity of isotactic polypropylene is ca. 100 J/g while its solubility in refluxing heptane is less than 3 wt%.

The polymer types mentioned in this presentation are shown in Table 1. Also shown in said table are the MV, NP and RBSP.

Heat Resistance

The shear adhesion failure temperature (SAFT) determines the temperature at which specimens bonded with HMA delaminate under static load in shear (2). Table 2 shows how the SAFT decreases as the concentration of ethylene increases in the copolymers. On the other hand, at constant ethylene concentration, e.g., the 2300 series, the SAFT increases with molecular weight. As can be seen in Table 2, the heat resistance is proportional to the softening point of the copolymer; higher softening point products show a correspondingly higher SAFT. So, two factors control the SAFT: polymer softness (determined by the polymer composition) and molecular weight.

Tensile Strength

Table 2 also shows the tensile strength (TS) of the APAO with the homopolymers showing the highest values. As the ethylene content in the copolymers increases, the TS decreases, very much in agreement with the increasing softness as measured by RBSP and NP. Within a particular series, the TS increases with molecular weight, up to a certain extent. In general, with increasing MW, the chain entanglements as well as the intrachain interactions increase. An apparent exception to this trend is the TS values for 2330 and 2385 which are quite similar to each other (as is their SAFT). 2780 did not yield, showing an elongation > 700 %.

Low Temperature Flexibility

A characteristic of these amorphous thermoplastic polymers is their low temperature flexibility. 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 will be used in a cold weather climate. The low temperature flexibility is related to the glass transition temperature (Tg) determined by DSC. Table 2 shows the Tg of APAO and it is evident that the softer the APAO the lower the Tg. As with other physical properties such as NP and RBSP, Tg is constant for a constant ethylene concentration, independent of the molecular weight, but it is dependent on the copolymer composition. The higher the ethylene concentration in the copolymer, the lower the Tg, the lower the temperatures at which the onset of molecular motion occurs. The higher the ethylene content in the copolymer, the higher the mobility of the polymer chains because the mobility is primarily determined by the barrier to rotation around backbone carbon-carbon bonds. Replacing a methyl group for a hydrogen atom decreases the barrier to rotation, therefore lowering the Tg. For a 1-butene copolymer, there is again a higher energy barrier to rotation but the somewhat longer alkyl substituent might actually plasticize the copolymer showing a lower Tg than the homopolymer.

Tack

Shown in Table 2 is the rolling ball tack, which measures the room temperature tackiness of a film of adhesive. Only the high ethylene copolymers show a R.B. Tack of less than 20 cm, the rest not exhibiting any meaningful room temperature tack.

APAO BLENDS

The hydrocarbon, aliphatic nature of these polymers limits their compatibility to compounds with a similar chemical nature. Modifiers for APAO include tackifiers and waxes. The tackifier gives tack and improves adhesion at application temperature by lowering the viscosity and improving wetting. The wax is used to reduce cost, lower viscosity, control setting time and reduce penetration. The compatibility of these modifiers with the APAO is important to the hot melt properties and processability.

Blends with Tackifiers

Table 3 shows data on compatibility of APAO with a variety of tackifiers. The compatibility, as determined by the Cloud Point (C.P.) of the blend, is highest with tackifiers of a aliphatic or alicyclic nature. Not unexpected, with aromatic

tackifiers, the blends show total incompatibility. With a rosin ester tackifier, APAO blends show limited compatibility requiring temperatures in excess of 160 C to show clear blends. In moving down any column on Table 3, it is evident that, in general, the C.P. of the binary blends decreases proportionally with the S.P. of the neat APAO. A higher C.P. is not so much indicative of increasing incompatibility as it is the result of increasing S.P. of the thermoplastic component. Differences in molecular weight is also a factor that influences the compatibility between two components as exemplified by the APAO/Escorez 5320 blend, vis-a-vis the APAO/Escorez 5300 blend.

The effect of temperature on the melt viscosity of different APAO/tackifier blends is shown in Fig. 2 while the effect of blend composition on APAO/tackifier blend NP and melt viscosities is shown in Fig. 3. Figure 3a shows that over a wide range of composition, the RBSP changes relatively little, less than 15 % for 2730 and less than 10 % for 2180. The RBSP of the tackifier is 98° C (208° F). On the other hand, as shown in figures 3b and 3c, the MV is highly sensitive to the blend composition, with the sensitivity, as determined by the slope of the plots, increasing as the temperature at which the MV is determined increases. This behavior should differ depending on the particular type of tackifier used as each resin has a different MV at the test temperature and all have a much lower viscosity than the APAO tested.

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.

Blends with Waxes

Compatibility of APAO with microcrystalline as well as with synthetic polyethylene waxes, as shown in Table 4, is excellent at high temperatures. At room temperature, the blends are opaque and the C.P. is determined by the softening point of the APAO.

Blends with Tackifiers and Waxes

The C.P. of ternary blends of APAO:tackifier:wax are shown in Table 5. It is interesting to note that the addition of microcrystalline wax to the APAO:Escorez 5320 blend makes for a more compatible blend.

Some APAO-based HMA Formulations

Table 6, shows a list of some hot melt adhesive formulations of commercial application.

SUMMARY

The APAO presented herein show a range of closely controlled properties which makes them highly desirable to be used in HMA formulations. The SAFT for a series is somewhat dependent on the molecular weight as well as, in general, to the softening points of the copolymers. All products can be considered as having comparatively low tensile strength, and as already discussed, the TS varies proportionally with the softness of the polymers.

The compatibility of blends with tackifiers and waxes is directly related to their chemical nature and to a certain extent to their molecular weight.

APPENDIX A

Test Methods

Melt viscosity	ASTM D-3236
Needle Penetration	ASTM D-1321
Softening Point	ASTM E-28
Rolling Ball	ASTM D-3121
Tensile Strength	ASTM D-638
Cloud Point	AMS 360.22
S.A.F.T.	TMHM-023
Open Time	REXENE Method

REFERENCES

1.- Business Research Report B149: Hot Melt Adhesives.
2.- ASTM D-4498

ACKNOWLEDGMENTS

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TABLE 1. AMORPHOUS POLYALPHAOLEFIN PRODUCT PROPERTIES

PRODUCT TYPE	POLYMER TYPE	BROOKFIELD VISC. (mPa.s)	NEEDLE PENET. (dmm)	SOFT. POINT °C (°F)
2115	Propylene	1500	15	152 (305)
2180	homopol.	8000	10	157 (315)
2215	Low ethyl.	1500	20	143 (290)
2280	copolym.	8000	15	146 (295)
2304	Medium	400	25	138 (280)
2315	ethylene	1500	25	138 (290)
2330	copolym.	3000	20	141 (285)
2385		8500	20	141 (285)
2535	High ethyl.	3500	45	129 (265)
2585	copolym.	8500	40	129 (265)
2715	1-Butene	1500	25	110 (230)
2730	copolym.	3000	25	107 (225)
2780		8000	25	107 (225)

TABLE 2. AMORPHOUS POLYALPHAOLEFIN PRODUCT PROPERTIES

PRODUCT TYPE	S.A.F.T. °C (°F)	T.S. MPa (PSI)	GLASS TRANS. °C (°F)	ROLL. BALL Tack (cm)
2115	132 (269)	2.30 (334)	-20 (-4)	)40
2180	139 (282)	2.56 (372)	-20 (-4)	)40
2215	112 (234)	0.87 (126)	-22 (-8)	)40
2280	113 (236)	1.09 (158)	-22 (-8)	)40
2304	99 (210)	0.49 (71)	-29 (-20)	)40
2315	101 (214)	0.57 (83)	-29 (-20)	)40
2330	112 (234)	0.82 (119)	-29 (-20)	)40
2385	113 (235)	0.79 (114)	-29 (-20)	)40
2535	83 (182)	0.35 (50)	-37 (-35)	20
2585	94 (201)	N.D.	-37 (-35)	18
2715	78 (173)	0.56 (81)	-23 (-9)	)40
2730	78 (172)	0.61 (89)	-23 (-9)	)40
2780	82 (180)	NO YIELD	-23 (-9)	)40

TABLE 3a. CLOUD POINTS OF APAO : TACKIFIER BLENDS

PRODUCT NAME	RING & BALL SOFT. POINT (°C)	C.P. BLEND A R.T.	C.P. BLEND A 190°C	C.P. BLEND B R.T.	C.P. BLEND B 190°C	C.P. BLEND C R.T.	C.P. BLEND C 190°C
2115	152	s.c. (100-105)	cl	s.c. (95 C)	cl	c (97-100)	cl
2180	157	s.c. (95-100)	cl	s.c. (98-103C)	cl	c (99-102)	cl
2215	143	s.c. (85-90)	cl	s.c. (96 C)	cl	c (85-86)	cl
2280	146	s.c. (91-93)	cl	s.c. (94-98 C)	cl	c (82-84)	cl
2304	138	s.c. (80-82)	cl	s.c.	cl	c (79-80)	cl
2315	138	s.c. (80-83)	cl	s.c.	cl	s.c. (79-80)	cl
2330	141	s.c. (80-85)	cl	s.c.	v.s.c.	s.c. (72-73)	cl
2385	141	s.c. (< 75)	cl	v.s.c.	v.s.c.	s.c. (75-78)	cl
2535	129	s.c. (@ 85)	cl	s.c. (85-90 C)	cl	v.s.c. < 70	cl
2585	129	s.c. (< 75)	cl	v.s.c.	cl	c < 70	cl
2715	110	s.c. (< 60)	cl	v.s.c.	cl	cl	cl
2730	107	s.c. (< 70)	cl	v.s.c.	cl	cl	cl
2780	107	s.c. (< 85)	cl	s.c.	cl	s.c.	cl

CONDITIONS: BLEND A: APAO : ZONAREZ 7115L = 1:1
B: APAO : WINGTACK 95 = 1:1
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 3b. CLOUD POINTS OF APAO : TACKIFIER BLENDS

PRODUCT NAME	RING & BALL SOFTENING POINT	C.P. BLEND D R.T.	C.P. BLEND D 190°C	C.P. BLEND E R.T.	C.P. BLEND E 190°C	C.P. BLEND F R.T.	C.P. BLEND F 190°C
2115	152	I	I	c	c	o	c
2180	157	I	I	c	c	o	c
2215	143	I	I	c	s.c.	o (187 C)	cl
2280	146	I	I	c	c	o	C
2304	138	I	I	c	v.s.c.	o (161 C)	cl
2315	138	I	I	c	s.c.	o (172 C)	cl
2330	141	I	I	c	c	o (169 C)	cl
2385	141	I	I	c	c	o	c
2535	129	I	I	c	v.s.c.	o (185 C)	cl
2585	129	I	I	c	s.c.	o (189 C)	cl
2715	110	I	I	c	c	o	c
2730	107	I	I	c	c	o	c
2780	107	I	I	c	c	o	c

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

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

TABLE 4. CLOUD POINTS FOR APAO : WAX BLENDS

PRODUCT NAME	RING & BALL SOFTENING POINT	C.P. BLEND A R.T.	C.P. BLEND A 190°C	C.P. BLEND B R.T.	C.P. BLEND B 190°C	C.P. BLEND C R.T.	C.P. BLEND C 190°C
2115	152	o (133 C)	cl	o (122 C)	cl	o (116 C)	cl
2180	157	o (123 C)	cl	o (123 C)	cl	o (118 C)	cl
2215	143	o (108 C)	cl	o (126 C)	cl	o (119 C)	cl
2280	146	o (121 C)	cl	o (117 C)	cl	o (118 C)	cl
2304	138	o (108 C)	cl	o (114 C)	cl	o (112 C)	cl
2315	138	o (104 C)	cl	o (112 C)	cl	o (105 C)	cl
2330	141	o (105 C)	cl	o (106 C)	cl	o (116 C)	cl
2385	141	o (103 C)	cl	o (93 C)	cl	o (110 C)	cl
2535	129	o (99 C)	cl	o (107 C)	cl	o (109 C)	cl
2585	129	o (101 C)	cl	o (95 C)	cl	o (106 C)	v.s.c.
2715	110	o (100 C)	cl	o (93 C)	cl	o (104 C)	v.s.c.
2730	107	o (99 C)	cl	o (93 C)	cl	o (106 C)	v.s.c.
2780	107	o (97 C)	cl	o (89 C)	cl	o (106 C)	v.s.c.

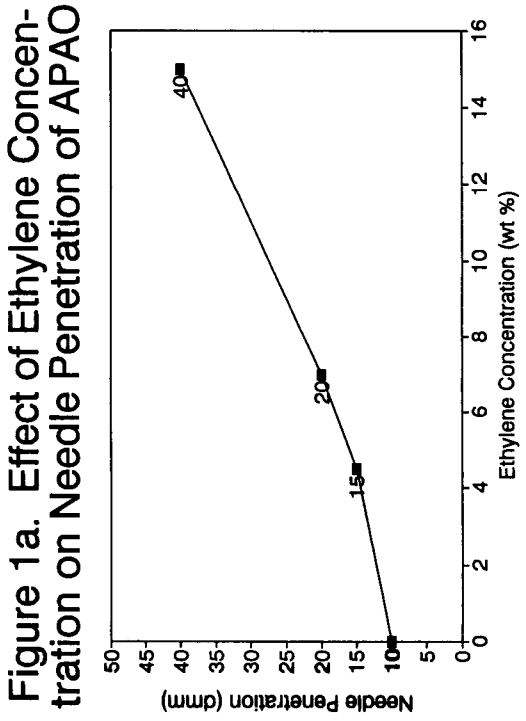
CONDITIONS: BLEND A: APAO : B SQUARE 185 = 1:1
B: APAO : MICROWAX 15 = 1:1
C: APAO : EPOLENE N11 = 1:1

TABLE 5. CLOUD POINTS FOR APAO:TACKIFIER:WAX BLENDS

PRODUCT NAME	RING & BALL SOFT. POINT (°C)	C.P. BLEND A R.T.	C.P. BLEND A 190°C	C.P. BLEND B R.T.	C.P. BLEND B 190°C	C.P. BLEND C R.T.	C.P. BLEND C 190°C	C.P. BLEND D R.T.	C.P. BLEND D 190°C
2115	152	o (114 C)	cl	o (102 C)	cl	o	o	s.c (90 C)	cl
2180	157	o (100 C)	cl	o (112 C)	cl	o	o	v.s.c. (79 C)	cl
2215	143	o (101 C)	cl	o (117 C)	cl	o	o	s.c. (81 C)	cl
2280	146	o (111 C)	cl	o (104 C)	cl	o	o	v.s.c. (91 C)	cl
2304	138	o (110 C)	cl	o (111 C)	cl	o	o	s.c. (69 C)	cl
2315	138	o (109 C)	cl	o (110 C)	cl	o	o	s.c. (77 C)	cl
2330	141	o (99 C)	cl	o (107 C)	cl	o	o	v.s.c. (73 C)	cl
2385	141	o (112 C)	cl	o (88 C)	cl	o	o	v.s.c. (67 C)	cl
2535	129	o (98 C)	cl	o (90 C)	cl	o	o	v.s.c. (53 C)	cl
2585	129	o (92 C)	cl	o (88 C)	cl	o	o	v.s.c.	cl
2715	110	o (92 C)	cl	o (86 C)	cl	o	o	v.s.c.	cl
2730	107	o (91 C)	cl	o (87 C)	cl	o	o	v.s.c.	cl
2780	107	o (89 C)	cl	o (89 C)	cl	o	o	v.s.c.	cl

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

cl = clear
v.s.c. = very slightly cloudy
s.c. = slightly cloudy
c = cloudy
o = opaque



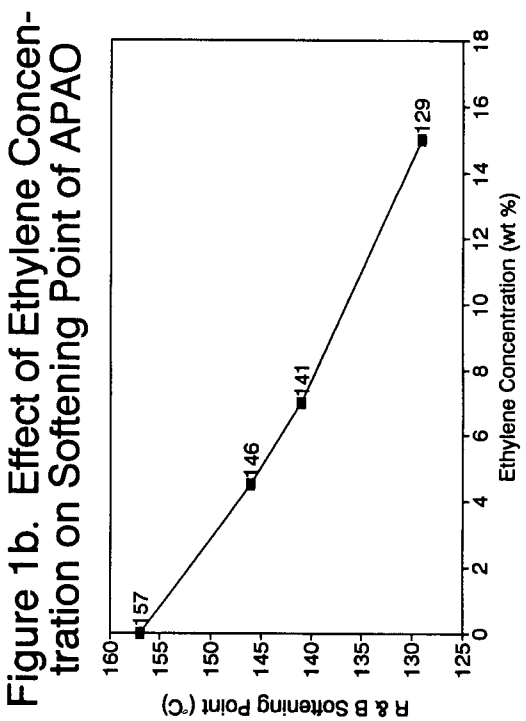


Fig. 3a. Effect of Composition of APAO Tackifier Blends on Softening Points

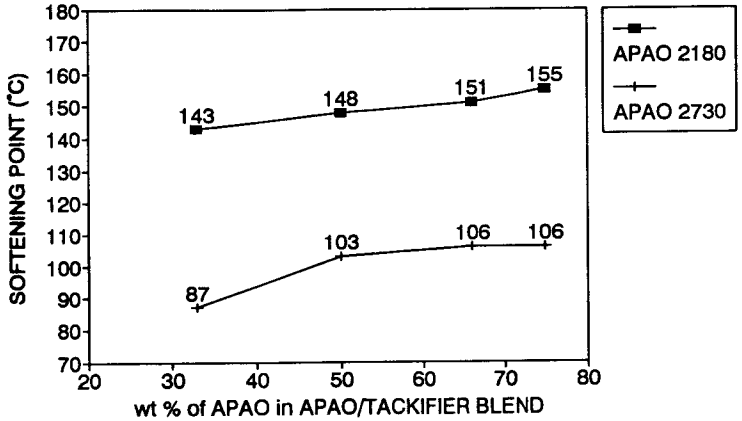


Fig. 2a. Effect of Temperature on the MV of 2180 : Tackifier blends

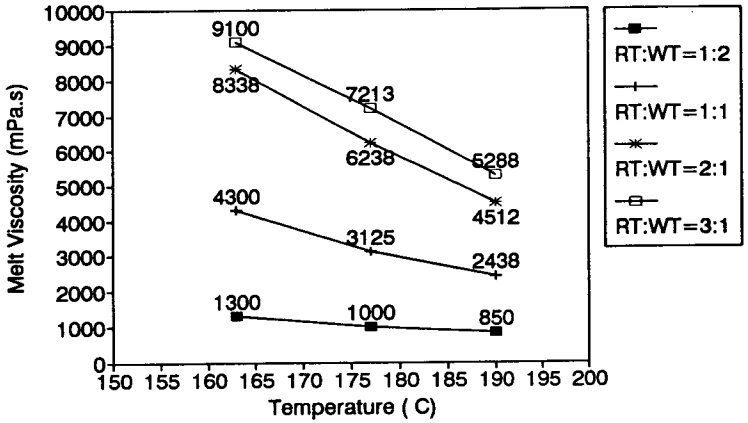


Fig. 3b. Effect of Composition of 2180/ Tackifier blends on Melt Viscosity

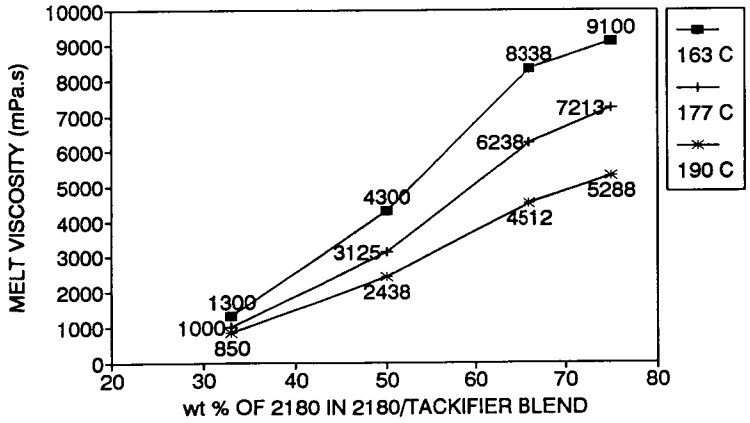


Fig. 2b. Effect of Temperature on the MV of 2730 : Tackifier blends

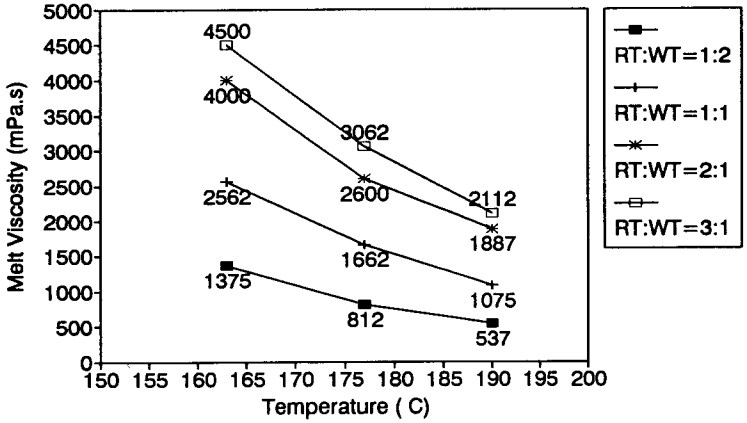


Fig. 3c. Effect of Composition of 2730/ Tackifier blends on Melt Viscosity

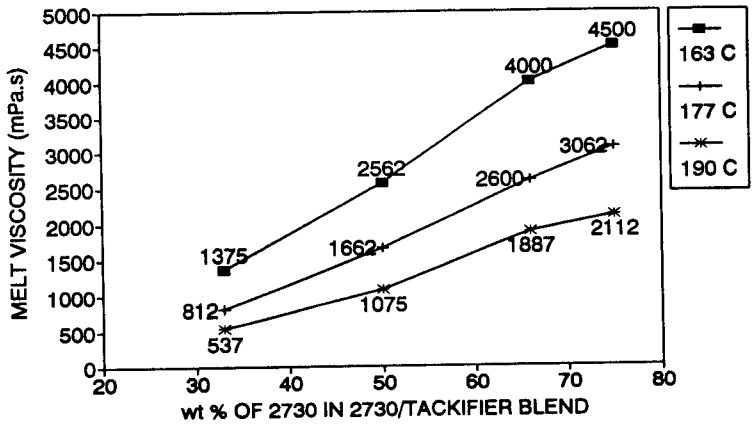


TABLE 6. APAO BASED HMA FORMULATIONS

ADHESIVE FOR PACKAGING

RAW MATERIALS	PERCENT BY WEIGHT
RT 2780	40
RT 2180	10
Escorez 1102	20
B-Square wax	30

PHYSICAL CONSTANTS	
Melt Viscosity (mPa.s)	605
Needle Penetration (dmm)	10
Softening Point °C (°F)	117 (243)
Cloud Point (°C)	R.T. 190°C s.c. cl
S.A.F.T. °C (°F)	72 (161)

MULTIPURPOSE ADHESIVE, MEDIUM OPEN TIME

RT 2780	70
Escorez 1102	30

Melt Viscosity (mPa.s)	3275
Needle Penetration (dmm)	25
Softening Point °C (°F)	103 (218)
Cloud Point (°C)	R.T. 190°C s.c. cl
Open Time (sec.)	60
S.A.F.T. °C (°F)	74 (165)

LAMINATING ADHESIVE FOR HIGHER REQUIREMENTS, MEDIUM OPEN TIME

RT 2280	80
ESCOREZ 5320	20

Melt Viscosity (mPa.s)	5500
Needle Penetration (dmm)	12
Softening Point °C (°F)	143 (289)
Cloud Point (°C)	R.T. 190°C o c
Open Time (sec.)	60
S.A.F.T. (°F)	118 (245)

ADHESIVE FOR MULTI-LINE APPLICATION FOR DIAPERS

RT 2780	61
ESCOREZ 5320	22
AMOCO H1500	12
AMOCO H100	5

Melt Viscosity (mPa.s)	2737
Needle Penetration (dmm)	36
Softening Point (°F)	101 (214)
Cloud Point (°C)	R.T. 190°C s.c. cl
Open Time (sec.)	600
S.A.F.T. °C (°F)	72 (161)

ADHESIVE FOR ASSEMBLY OF DIAPERS

RT 2780	65
RT 2115	15
ESCOREZ 5300	20

Melt Viscosity (mPa.s)	3625
Needle Penetration (dmm)	22
Softening Point °C (°F)	132 (270)
Cloud Point (°C)	R.T. 190°C s.c. cl
Open Time (sec.)	60
S.A.F.T. °C (°F)	87 (189)